PROCEEDINGS OF THE WORKSHOP

ON

AQUATIC FOOD CHAIN MODELLING

ORGANIZED BY

YOUSRY HAMDY and GARY JOHNSON

ONTARIO MINISTRY OF THE ENVIRONMENT
TORONTO, ONTARIO, CANADA, M4V 1P5

AND

J.A.McCORQUODALE

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WINDSOR, ONTARIO, CANADA, N9B 3P4

JULY 9, 10, 1987 AT
EATON HALL, SENECA COLLEGE
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MEMORANDUM

TO: Distribution List

FROM: J. N. Bishop
Director
Water Resources Branch

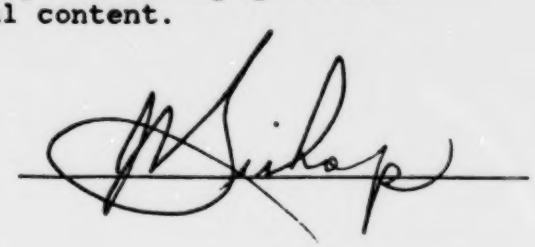
RE: **WORKSHOP - AQUATIC FOOD CHAIN MODELLING**
SENECA COLLEGE

Enclosed is a copy of the proceedings of a workshop on Aquatic Food Chain Modelling held at Seneca College, King City, Ontario on July 9-10, 1987. The workshop was organized by the Water Resources Branch of the Ministry of the Environment in co-operation with the University of Windsor.

The workshop encouraged a healthy exchange of information between biologists, chemists and modellers and led to the formulation of a generic model to be used as a tool for screening impacts of discharges on river and lake ecosystems. The workshop also identified research needs for the development of site-specific food chain models.

With reference to Chapter 1 dealing with the MISA Water Quality Track, a note of clarification is needed. At the time of the July workshop, it was assumed that both the Best Available Technology Economically Achievable (BATEA) and Water Quality Tracks of MISA would be developed simultaneously. As a result of decisions on MISA's direction that took place after the July Workshop, the Water Quality Track will now be applied in a sequential fashion, after the monitoring and effluent regulations have been promulgated. This decision reflects the time required for detailed technical regulations with industry, the MISA Advisory Committee and the general public, and the need for speedy completion of the monitoring and effluent limits regulations. The Water Quality Track, however, continues to be recognized as an essential component of the Ministry's developing regulatory and control program.

I trust that you will find these proceedings to be informative. You may wish to contact the various authors directly should you have any questions concerning the technical content.



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SOMMAIRE

On a tenu un atelier les 9 et 10 juillet 1987 dont l'objectif était d'élaborer un sous-modèle de la chaîne alimentaire aquatique qui serait incorporé au modèle du sort des polluants et au modèle du transport des polluants qui font partie de la SMID. Au cours des discussions en groupe et des exposés faits par les conférenciers invités, on a dégagé un certain nombre de concepts. En ce qui concerne la modélisation de la chaîne alimentaire, les produits chimiques qui s'accumuleraient dans les organismes vivants ont été isolés en tant qu'éléments critiques.

Les participants aux séances en petits groupes ont convenu de créer un modèle de base de la chaîne alimentaire, qui comprendrait quatre ou cinq niveaux trophiques basés sur la taille des organismes. Ils ont également convenu d'utiliser ce modèle comme instrument de tri des produits chimiques pour déterminer s'il faut se préoccuper, dans des endroits précis, du processus de bio-accumulation. Les participants ont insisté sur l'importance de commencer l'élaboration d'un modèle spécifique pour un site contrôle, à partir des données connues.

OPENING REMARKS

BY

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Welcome to the Food Chain Modelling Workshop.

In June 1986 the Ontario Ministry of the Environment announced the Municipal Industrial Strategy for Abatement (MISA) program in order to eliminate discharges of persistent toxic contaminants to our waterways. The concept of virtual elimination stated in the MISA white paper focused on the challenge of dealing effectively with the increasing presence of toxic contaminants in Ontario's lakes and rivers.

Events such as those associated with the perchloroethylene spill in the St. Clair River and the presence of dioxin and mirex in the Niagara River prompted the attention of scientists to the fate and behaviour of toxic contaminants in the aquatic environment.

In this workshop we will focus on the fate of organics such as chlorinated benzenes, PCBs, polyaromatic hydrocarbons and dioxins. In general, such organic toxic contaminants pose a risk to fish, plants and other wild life and even man at low concentrations. They are persistent, accumulate in the environment and can be biomagnified in the food chain, thereby resulting in fish contaminant levels which may be thousands of times higher than in the water.

The development and application of food chain modelling serves as a valuable tool to provide a capability for testing hypotheses, identifying missing or poorly understood processes and integrating factors related to the fate of toxics. These models will provide service throughout the entire resource management process beginning with the problem definition and culminating in the selection of effective management options.

As a minimum requirement, the MISA white paper indicated that the Best Available Technology Economically Achievable (BAT-EA) will be used to establish effluent limits for industrial and municipal sectors. The

application of BAT will not always provide sufficient control of discharges to prevent adverse effects on the ecosystem.

We therefore must use models as tools to predict with a high degree of accuracy the fate and effect of loadings and concentrations of trace organics on each ecosystem compartment and to ensure compliance with water quality objectives and guidelines for aquatic life, wild life and public health over the short and long term. Monitoring of ecosystem compartments will require the collection of data on effluent quality, water quality, sediments (both active and non-active layers), phyto- and zoo-plankton, benthic community (taxa and body burden) and fish. We hope that the total picture can be obtained from an in-depth understanding and description of the food chain and the associated model application. These descriptions are the goal of this workshop.

ORGANIZATION OF THE WORKSHOP

In order to focus the workshop, several formal seminars were presented on the first day of the workshop (see attached programme). These seminars addressed both the fundamental questions of uptake as well as state-of-the-art food web modelling. The formal seminars were followed by work sessions. These were organized into three groups, namely:

1) plankton
2) fisheries
3) sediment/benthos.

The participants and coordinators of these work groups are shown on the attached list. Dr. McCorquodale and I participated in all three groups.

A coordinators meeting was held at the end of the first day.

The coordinators reported the findings of their respective group to the groups as a whole on the final day of the workshop. These findings and the ensuing discussion are summarized by J.A. McCorquodale in Chapter 8.

Several handouts (see samples attached in Appendix A) were prepared to help focus the discussion of the work groups.

CHAPTER 1

MISA WATER QUALITY TRACK

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INTRODUCTION

In June 1986 the Ontario Ministry of the Environment announced the MISA - "Municipal-Industrial Strategy for Abatement" - program. This new approach to controlling point-source water pollution has an ultimate goal the virtual elimination of toxic contaminants from all industrial and municipal effluents discharged into the province's waterways. The program is being developed in consultation with Environment Canada, industries, interest groups and the general public.

For the first time in Ontario, there will be regulations to limit loadings of trace organic and inorganic substances to surface waters. For each of the major sectors of industry and the municipal sector, two regulations will be developed. Initially, dischargers will be subject to Monitoring and Reporting Regulations which will require them to identify, measure and, report on concentrations and amounts of toxics in their effluents. Minimum legal requirements for the submission, accuracy and reliability of self-monitoring information, including specifications for sampling and analytical protocols and quality assurance and quality control procedures, will be set. This self-monitoring program will be audited by the Ministry of the Environment.

This initial monitoring phase will be followed by Compliance or Limits Regulations that will specify allowable concentrations, as well as amounts or loadings, of toxic pollutants for each discharger. This will be done on a sector-by-sector basis and the specified levels will be based on the Best Available Technology Economically Achievable (BATEA).

Joint technical committees for each industrial sector and the municipal sector will negotiate practical and effective requirements for each regulation.

More stringent effluent limits may be required for specific sites to protect sensitive water bodies. This action would occur in cases where water quality assessments show that controls beyond those required by BATEA may be necessary to protect the environment (Fig. 1.1).

The BATEA and Water Quality tracks are complementary in nature. This interrelationship will enable the implementation of effective controls with impact on the environment being the final determinant.

MISA WATER QUALITY TRACK

The Ministry is undertaking a major review and revision of its traditional water quality impact approach to enhance the province's capability to assess ecosystem response to municipal and industrial discharges.

These evaluations include:

i) The development of ambient water quality objectives (PWQO) for many additional toxic substances. This will involve updating "Blue Book" ambient numerical and narrative requirements to protect water quality; (Fig. 1.2);

ii) The revision of policies and procedures for the Water Quality based approach to pollution control;

iii) The development of testing techniques to assess the impacts of toxics at selected pilot sites;

iv) The development of precepts for controlling toxic discharges;

v) The definition and staging of virtual elimination of toxic contaminants entering our waterways;

vi) The development of a relatively simple screening process to determine whether BATEA-controlled discharges within a given sector will meet receiving water requirements;

vii) The selection and validation of biological effluent testing procedures to determine acute and chronic toxicity, genotoxicity and bioconcentration;

viii) The development of acceptable guidelines for sediment and biota.

The competition of these components will allow identification of situations where more stringent effluent limits are called for, the application of approval assessment procedures and development of effluent requirements based on water quality impacts on a site-specific basis.

Following an initial screening process, discharges requiring more in-depth receiving water assessments will be subject to intensive site-specific modelling efforts to establish local impacts and related controls. Fate and transport models now evolving through exercises such as this workshop will be essential to determine far-field concentrations, partitioning and potential aquatic effects.

Looking to the future, whole lake effect modelling must be integrated with toxocity and bioconcentration assessments as a basis for prioritization of sources and related controls. Satisfactory and points for toxic contaminants must be established to permit trend-through-time evaluations at critical locations as a means of monitoring the success of remedial efforts and maintaining vigilance on the integrity of the aquatic ecosystem.

FIGURE CAPTIONS

Fig. 1.1. Technology and water quality tracks.

Fig. 1.2. The revised blue book will be the expression of the Ministry's Water Quality Management Program including MISA's principles, policies, objectives, and ambient and discharge requirements.

EFFLUENT LIMIT DERIVATION

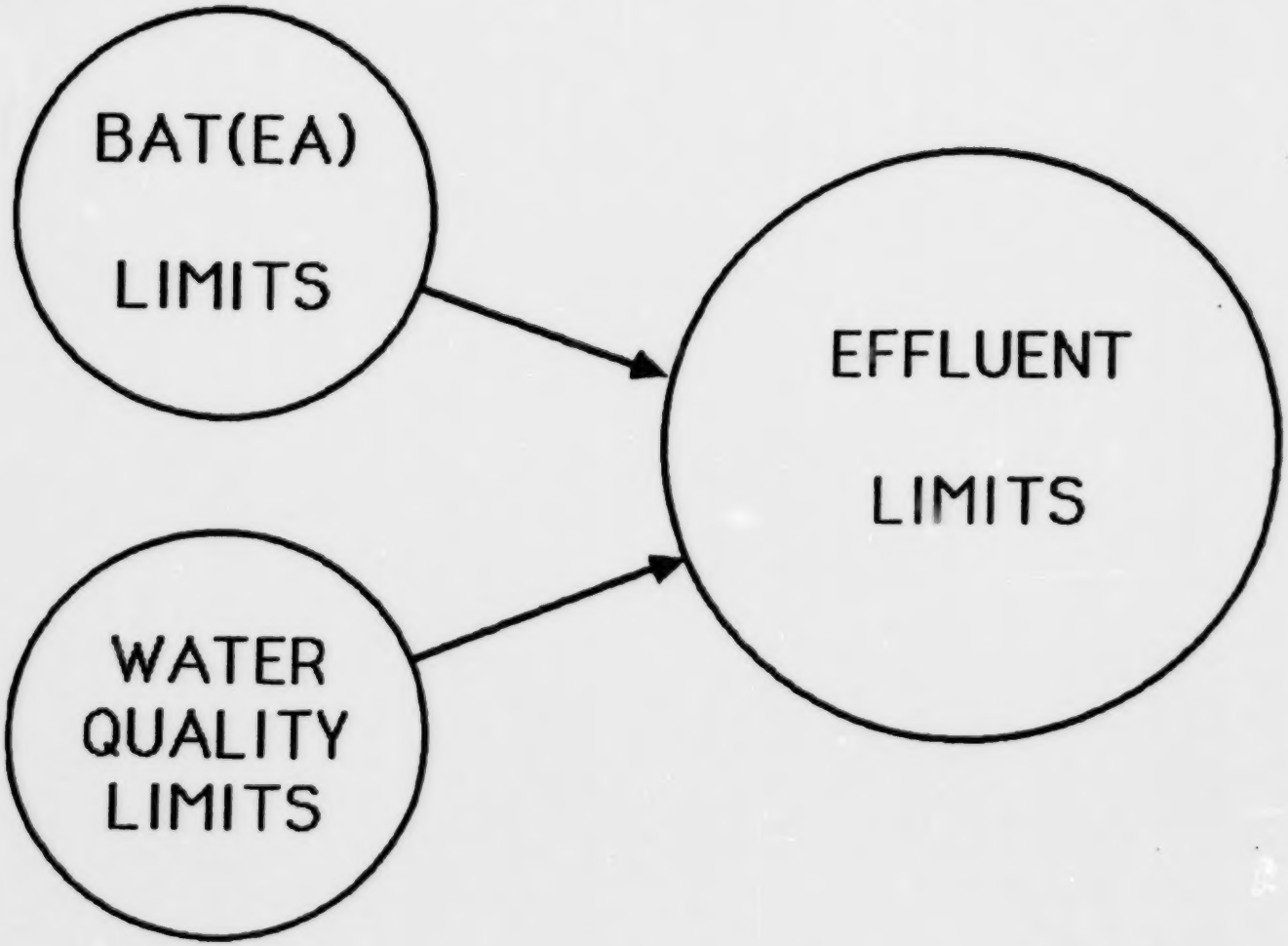

FIG. 1.1 Technology and Water Quality Tracks

The Water Quality Track is one of the two major components of MISA:

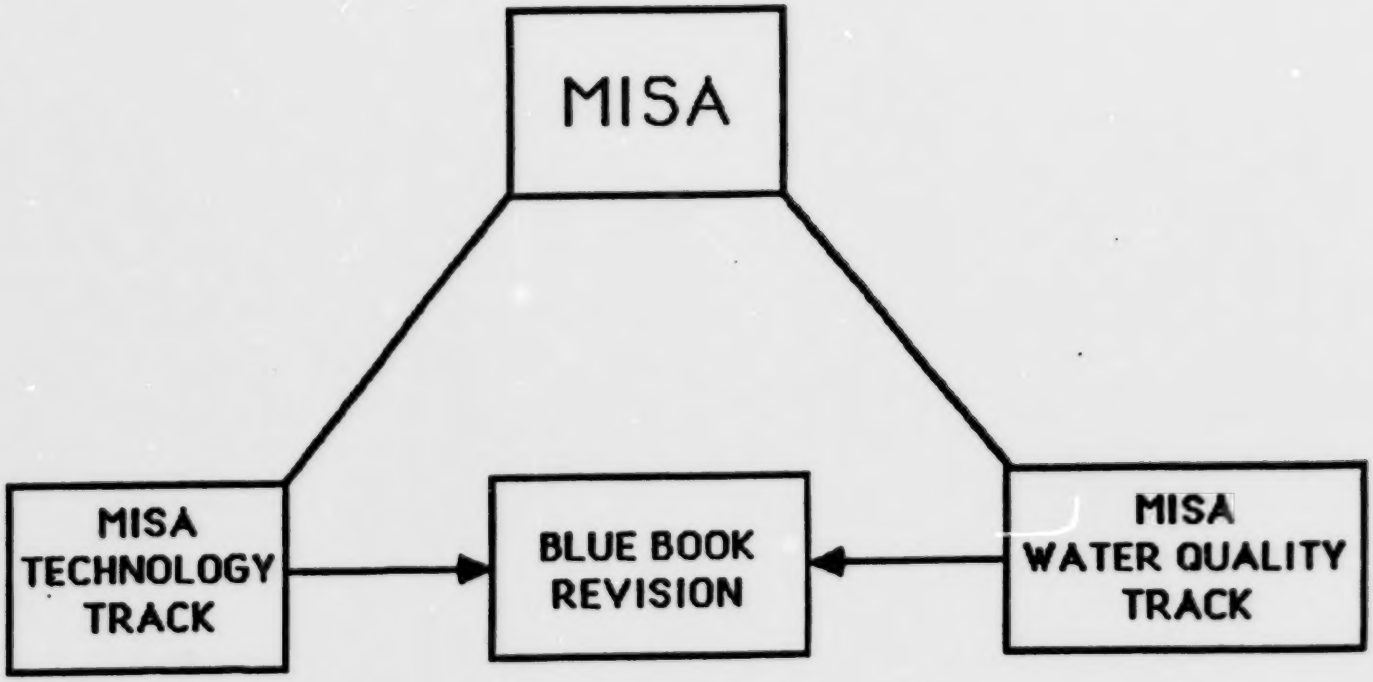

FIG. 1.2 The revised Blue Book will be the expression of the Ministry's Water Quality Management Program including MISA's principles, policies, objectives, and ambient and discharge requirements.

CHAPTER 2

A MODELLING FRAMEWORK FOR ESTIMATING CONTAMINANTS LEVELS IN BIOTA

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OBJECTIVE

This workshop was organized to exchange information between Great Lakes aquatic biologists and water quality modellers. The objective of the workshop was to suggest a food chain/web modelling framework that could be developed and tested within the MISA programme.

Figure 2.1 shows a sample of a generic food web of the type that can be handled by state-of-the-art "food chain" models. Figure 2.2 shows a chart for the preparation of a predator-prey diet distribution matrix. Specific questions that were directed to each work group are shown in Appendix A).

GENERAL BACKGROUND

The early water quality models were developed to answer questions related to the definition of zones of severe or even toxic impacts. These models considered primarily the near field mixing and far field dispersion processes. Questions of partitioning to solids and uptake in biota were not considered. Such models were and still are useful in evaluating Limited Use Zones (LUZ) for conventional pollutants, e.g. TDS, un-ionized ammonia, and residual chlorine. However, these models are completely inadequate for organic toxics and certain heavy metals which partition to the sediment and are accumulated in the biota.

A new generation of models are now being developed which eventually will allow us to trace the fate of a contaminant from its source to the top of the food chain. These new models require a vast data base which includes measurements of mass loading and concentrations in ambient water, suspended sediment, bed sediment as well as in the biota at all trophic levels. In addition, the physical and chemical properties of the contaminant must be known.

MODELLING FRAMEWORK

The first step in any modelling exercise is the selection of the appropriate model that will best answer the questions related to a particular management decision; for example, what is the load allocation which will satisfy the provincial water quality objectives for ambient water, sediment, and sports fish?

All higher level surface water quality models consist of three components:

a) an hydrodynamic submodel,

b) an exposure submodel,

c) a biota uptake submodel.

A systems diagram showing these components is given in Fig.2.3.

HYDRODYNAMIC SUBMODEL

Only a brief description of hydrodynamic modelling can be included here. These models may be one, two- or three-dimensional in space and may be steady or unsteady. There are a number of available and documented models that can be used in the Great Lakes System. The US EPA supports a general unsteady network type hydrodynamic model called DYNAHYD3 (Ambrose et al. 1986). A simple two-dimensional steady-state model for large rivers has been developed at the University of Windsor (McCorquodale et al. 1987); this model is referred to as the k-E model. It is based on the work of Rastogil and Rodi (1978) and Krishnappan and Lau (1983) and provides velocities and dispersion coefficients on a variable grid across and along a river. There are a number of finite element and finite difference models available for computing circulation in the Great Lakes (Schwab et al. 1981, Simmons 1971 and Ibrahim and McCorquodale 1985).

Exposure Submodels

Exposure models are mass balance models which attempt to account for transport, partitioning, degradation and loss of any contaminant introduced to the system (see Fig. 2.4). These models are meant to give estimates of the ambient contaminant levels in all compartments of the lake or river.

In order to accomplish this, it is essential to know the physical and chemical properties of the pollutant. Some of these properties are: the octanol-water partition coefficient, the organic carbon partition coefficient, the molecular weight of the chemical, the Henry's law constant, the vapour pressure of the compound, the specific gravity, and the aqueous solubility of the toxicant chemical species. Other useful information for prediction are: bacterial population density in water, bacterial population density in bed sediments, concentration of solids in bed sediments, concentration of solids in the water column, the size distribution of the solids in the water column and the size distribution of the solids in the river bed, and the organic carbon content of the bed sediment.

Generally speaking the volatilization and decay mechanisms are important for long term considerations especially when flow enters slow moving bodies such as lakes. A thorough discussion of decay mechanisms is given in the EPA Reports dated June 1985 and March 1983. The major mechanisms include: volatilization, photolysis, hydrolysis, biodegradation, oxidation, and reduction.

There are several documented exposure models that have been applied for the Great Lakes System. Some of these are shown in Table 1. A

typical example is the EPA TOXIWASP model (Ambrose et al. 1983) which incorporates the features of WASP (DiToro et al. 1981) and EXAMS (Burns et al. 1982) including sediment-water interaction. Moreover it had already been used for toxic chemicals in a Great Lakes environment (Great Lakes Institute 1984).

The hydrodynamics for TOXIWASP can be obtained from DYNAHYD3 or from the k-E model described above. TOXIWASP includes the main mass transfer mechanisms to account for the interactions between dissolved chemical both with suspended solids and with stationary sediments in the river bed. These mechanisms, as shown in Fig. 2.5, include:

a) advection and dispersion of dissolved contaminants,

b) sediment contributions from point/nonpoint sources of solids and contaminants into the water,

c) volatilization and biological degradation.

The TOXIWASP model treats volatilization by the two film concept that is used by its predecessor, EXAMS (Burns et al. 1982).

The TOXIWASP model is a cell model which assumes that:

a) all segments are well mixed,

b) sorption is an instantaneous process within each segment,

c) the chemical properties of the compound can be coupled with the characteristics of the environment to formulate a first order reaction for the degradation process,

d) all the first order rates can be combined linearly.

Within each cell the elementary mass balance equation is solved to yield the time variable mass and concentration in each cell. Figure 2.6 shows schematically the partitioning of the total contaminant between the dissolved and particulate phases.

Figure 2.7 shows a typical schematic of the TOXIWASP cell arrangement: the number refers to the water column cells, the corresponding active and deep bed cells.

The Food Chain Submodel

The purpose of the food chain model is to relate the body burden in various trophic levels within the food chain to the prevailing or anticipated ambient contaminant levels.

Food chain models vary greatly in sophistication and data requirements. The following are some of the choices to be made in the selection and development of a model to predict body burdens in biota:

a) simple partitioning (BCF x ambient concentration), or a food web including uptake from water and food sources,

b) the model can be either steady or unsteady (dynamic),

c) in addition, a particular species can be treated by age or size classification,

d) the food chain submodel can be uncoupled or coupled to the exposure model,

e) the food chain model can be treated as a pathway (predator/prey) system or as a complete energy and mass balance system.

One of the simplest biotic contaminant models was proposed by Whitmore (1977) as illustrated in Fig. 2.8. This model uses simple partitioning between the dissolved and biotic phases.

Neely (1977) proposed a similar model (illustrated in Fig. 2.9) which attempted to predict contaminant levels in fish based on uptake and clearance rates. His model included a reasonable representation of the fate of a contaminant in the water phase.

Chapra (1982) proposed a comprehensive food web model as illustrated in Fig. 2.10. This model is generic in nature but includes both pelagic

and benthic components of the food chain. He included the following transfer processes:

a) flushing,
b) loading,
c) settling,
d) diffusion,
e) burial,
f) harvest,
g) sorption,
h) feeding,
i) uptake,
j) release,
k) egestion,
l) vaporization.

Manhattan College (Connolly et al. 1986) has developed a comprehensive modelling framework for a food chain which is represented schematically in Fig. 2.11. Their model (WASTOX) can be run in several modes, for example, as a food chain model with steady or unsteady exposure levels obtained from field measurements or their exposure model or any other appropriate exposure model such as TOXIWASP. WASTOX can accommodate several trophic levels (predator/prey relationships) with interaction at a number of levels, age classification within a species, migration of species within a cell structure, growth of the species, as well as unsteady loads and exposure levels. Furthermore, this model can be developed as a generic model or with sufficient site data it can be developed as a site-species specific model.

Thomann (1987) gives the rate equation used in the WASTOX food chain model as,

$$\frac{d\nu_i}{dt} = K_{ui}C_D + \sum_{j=1} a_{ij}C_{ij}\nu_j - K_i'\nu_i \qquad (1)$$

Uptake From Water	Uptake From Food	Growth and Excretion

in which v_i = biota contaminant concentration in species i

c_D = dissolved concentration

K_{ui} = uptake or BCF

α = assimilation efficiency of contaminant,

C_{ij} = consumption of species j by species i

K_i' = net growth + excretion rates for species i

A PROPOSED PATHYWAY FOOD MODEL

In order to progress towards a realistic food chain model the food web system shown in Fig. 2.1 is proposed as a starting point for discussion. This system can be accommodated by WASTOX provided that we have sufficient knowledge about the following:

a) the exposure levels for the selected contaminant,

b) the KOW of the contaminant,

c) the growth characteristics of the species of interest,

d) the respiration rates for the selected species.

e) the excretion rates for the selected species,

f) the lipid fractions of the selected species,

g) the migration patterns for all selected species,

h) the predator/prey relationships for all selected species,

i) biota mass by species and age classification.

The feeding relationships can be summarized on a consumer food matrix chart such as the one illustrated in Fig. 2.2.

Figure 2.12 lists a number of factors that a food web model should include. Many of these need further quantification through field and laboratories research before they can be adequately included in a mathematical model.

REFERENCES

Ambrose, R.B., Hill, S.I., and Mulkey, L.A., (1983).. "TOXIWASP User's Manual", US EPA ORD, Athens, Georgia, 30613.

Ambrose, R.B., Vandergrift, S.B., and Wool, T.A., (1986). "WASP3, A Hydrodynamic and Water Quality Model - Model Theory User's Manual, and Programmer's Guide", US EPA, Athens, Ga., EPA/600/3-86/034, Sep.

Bowie, G.L., Mills, W.B., Porcella, D.B., Campbell, C.L., and Chamberlin, C.E., (1985). "Rates, Constants, and Kinetics Formulations in Surface Waters", US EPA/600/3-85/040 Second Edition, Athens, Georgia, 30613.

Burns, L.A., Cline, D.M., and Lassiter, R.R., (1982). "Exposure Analysis Modeling System (EXAMS)", US EPA/600/3-023, Athens, Georgia, 30613.

Chapra, S.C., (1983). "Long-term Models of Interactions Between Solids and Contaminants in Lakes", Ph.D. Dissertation, University of Michigan, Ann Arbor, MI.

Connelly, J., and Winfield, R.P., (1986). "WASTOX, A Framework for Modelling the Fate of Toxic Chemicals in Aquatic Environment, Part I: Exposure Concentration", Draft Report for US EPA Environmental Research Laboratory, Gulf Breeze, Florida.

DiToro, D.M., Fitzpatrick, J.J., and Thomann, R.V., (1982). "Water Quality Analysis Simulation Program (WASP) and Model Verification Program (MVP)", Hydroscience Inc. for US EPA Diluth, Minnesota.

Great Lakes Institute, (1986). "Surface Water Transport - Task Group VI", Part of Report on DSS Contract of Case Study of Pb, Cd, OCS, and PCB in the Essex County Region, GLI University of Windsor, Windsor, Ontario, N9B 3P4.

Halfron, E., (1986). "Modeling the Pathways of Toxic Contaminants in the St. Clair-Detorit System Using TOXFATE Model: The Fate of Perchloroethylene", Water Poll. Res. J. Canada, Vol. 21, No. 3.

Ibrahim, K., (1986). "Simulation of Pollutant Transport in Lake St. Clair and Connecting Channels", Ph.D. Dissertation, University of Windsor, Windsor, Ontario, N9B 3P4.

Krishnappan, B.G., Lau, Y.L., (1983). "RIVMIX Transport Model", Computer Program Developed at CCIW, Burlington, Ontario.

McCorquodale, J.A., Iman, E., Bewtra, J.K., Hamdy, Y.S., and Kinkead, J., (1983). "Transport of Pollutants in Natural Streams", CJCE, Vol. 10, No. 1.

McCorquodale, J.A., and Ibrahim, K., (1984). "Niagara River Pollutant Transport", University of Windsor IRI Report To MOE, Toronot, Ontario.

McCorquodale, J.A., Ibrahim, K., and Hamdy, Y.S., (1986). "Fate and Transport Modelling of Perchloroethylene in the St. Clair River", Water Poll. Res. J. Canada, Vol. 21, No. 3.

Neeley, W.B., (1977). "A Material Balance of PCB's in Lake Michigan", Sci. Total Environment, Vol. 7, 117-129.

Rastogil, A.K., and Rodi, W., (1978). "Prediction of Mass and Heat Transfer in Open Channels", J. Hyd. Div., ASCE, HY3.

Ontario Ministry of the Environment and Environment Canada, (1986). "St. Clair River Pollution Investigation", A joint study.

Thomann R.V., (1987). "Principles of Surface Water Quality Modeling and Control", Harper and Row, Publishers, New York.

Whitmore, F.C., "A First Order Mass Balance Model for the Sources, Distribution and Fate of PCB's in the Environment", EPA-560/6-77-006, US EPA, Washington, D.C., 180 pp.

FIGURE CAPTIONS

Fig. 2.1. System diagram for a generic aquatic food chain model.

Fig. 2.2. Predator-prey diet matrix.

Fig. 2.3. A systems diagram for a complete surface water quality model (Hague, 1980).

Fig. 2.4. Typical transfer processes in exposure models.

Fig. 2.5. Processes in the TOXIWASP exposure model (Ambrose, 1983).

Fig. 2.6. The partitioning process in an exposure model.

Fig. 2.7. A typical planwise cell discretization for TOXIWASP.

Fig. 2.8. The Whitmore model (Chapra, 1983).

Fig. 2.9. The Neeley model (Chapra, 1983).

Fig. 2.10. The Chapra model (1983).

Fig. 2.11. The Manhattan College model, WASTOX (Connelly, 1986).

Fig. 2.12. Some factors that affect the contaminant uptake and accumulation in biota.

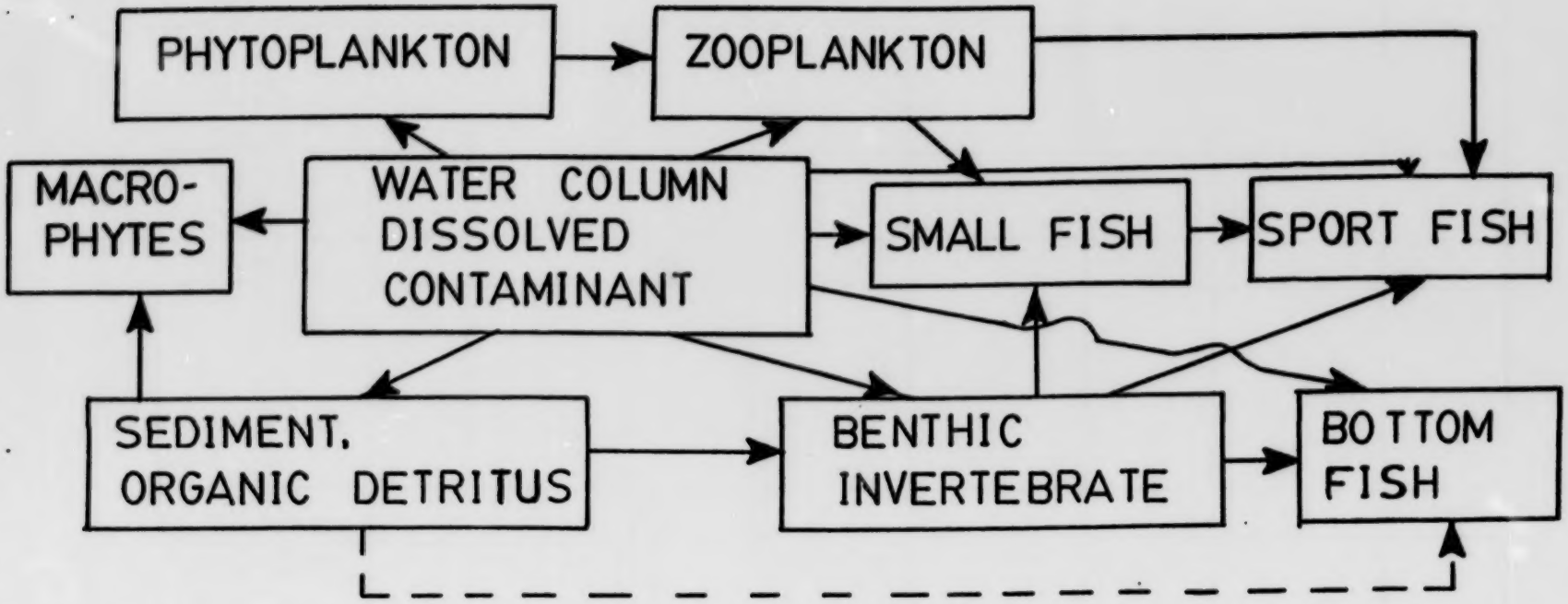


FIG. 2.1 System Diagram for a Generic Aquatic Food Chain Model

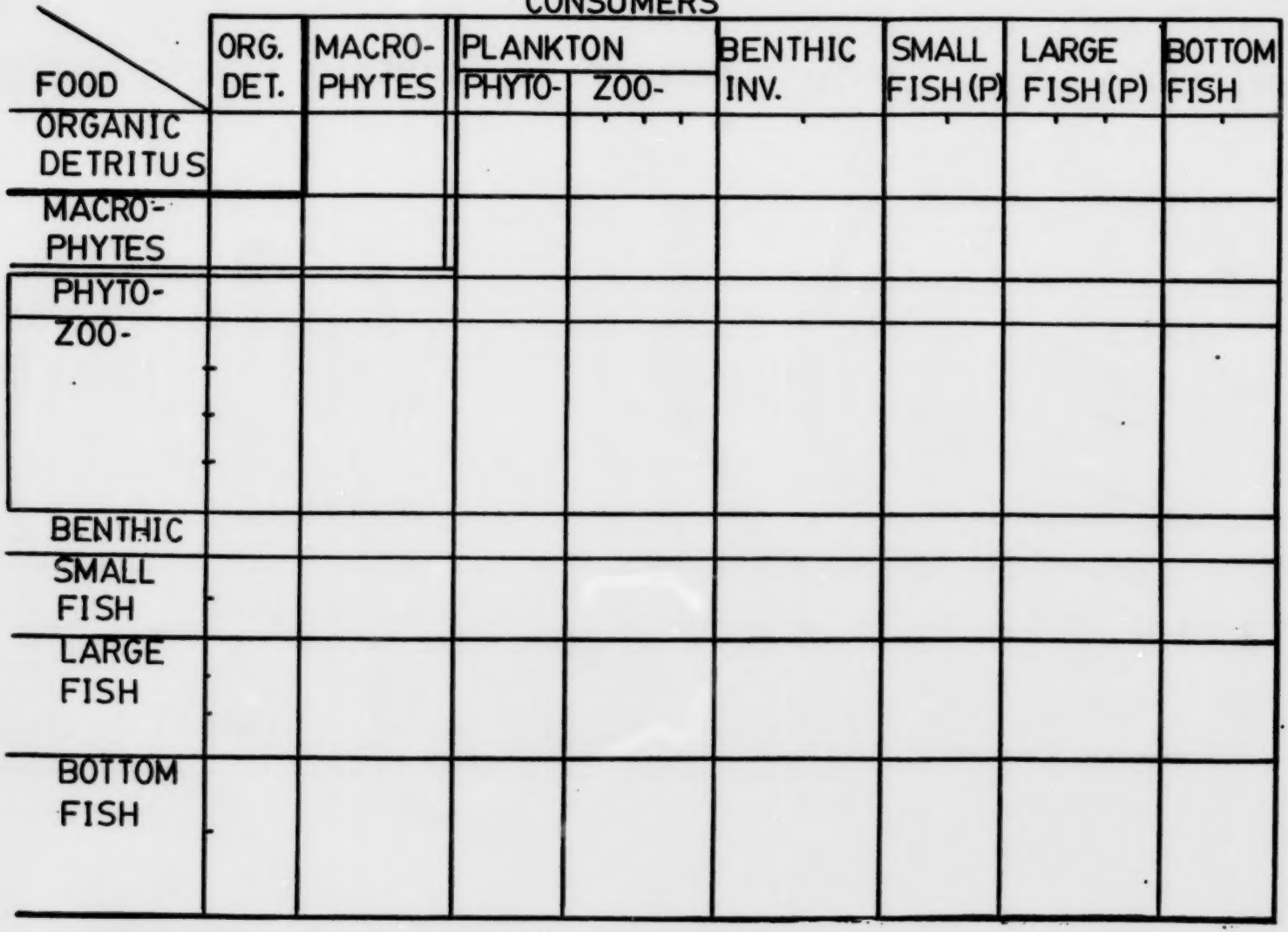


FIG. 2.2 Predator-Prey Diet Matrix

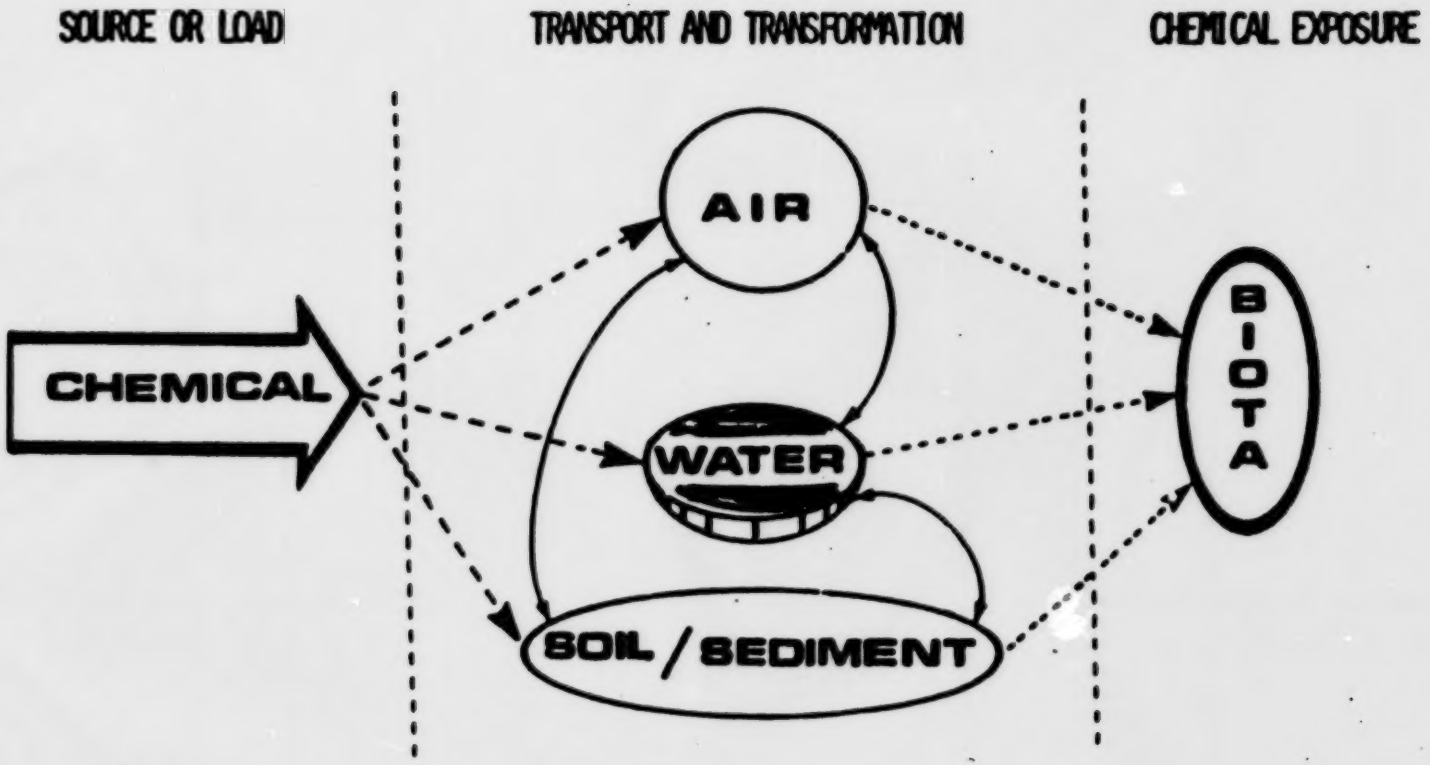


FIG. 2-3 A Systems Diagram for a Complete Surface Water Model (Hague, 1980)

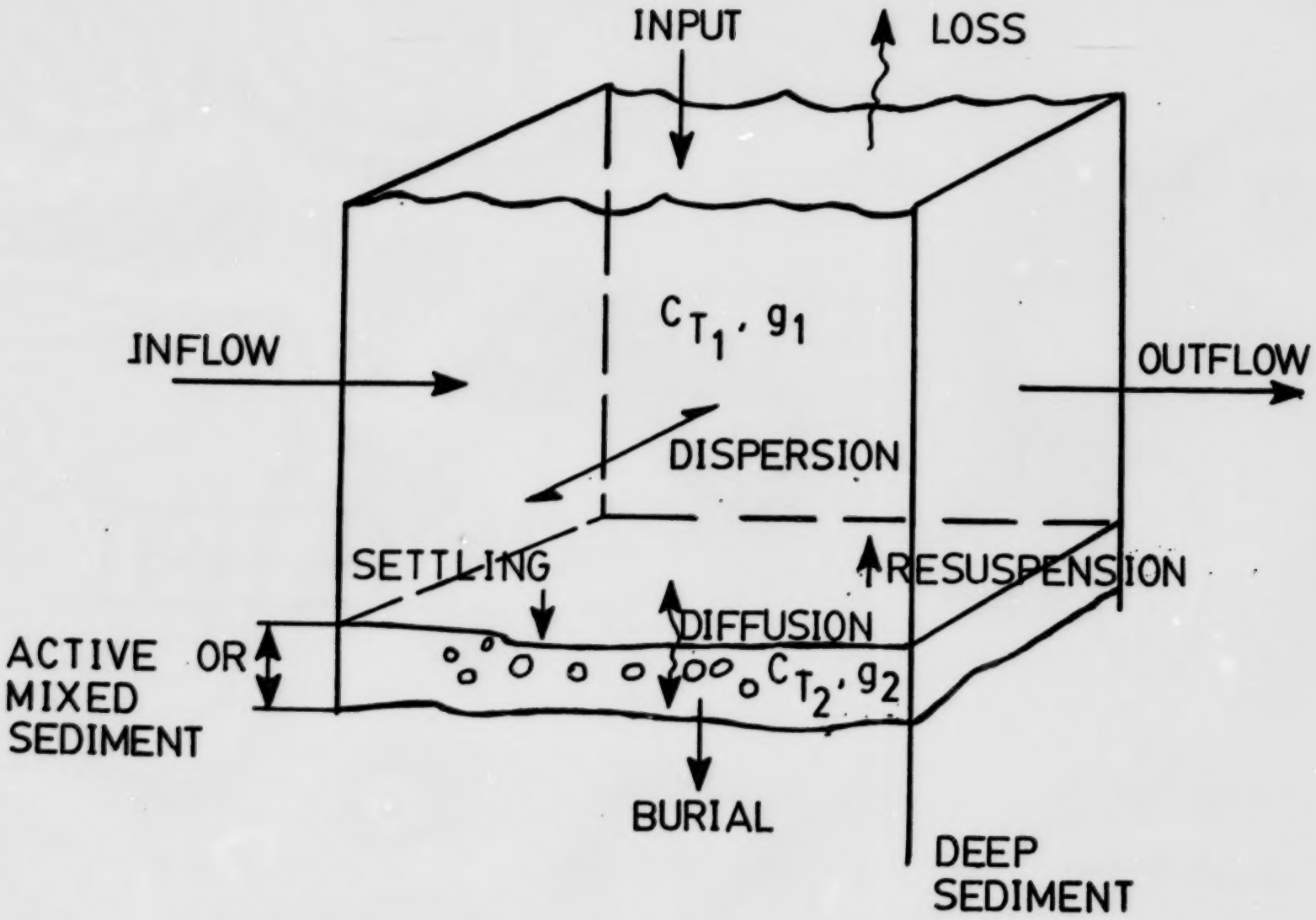
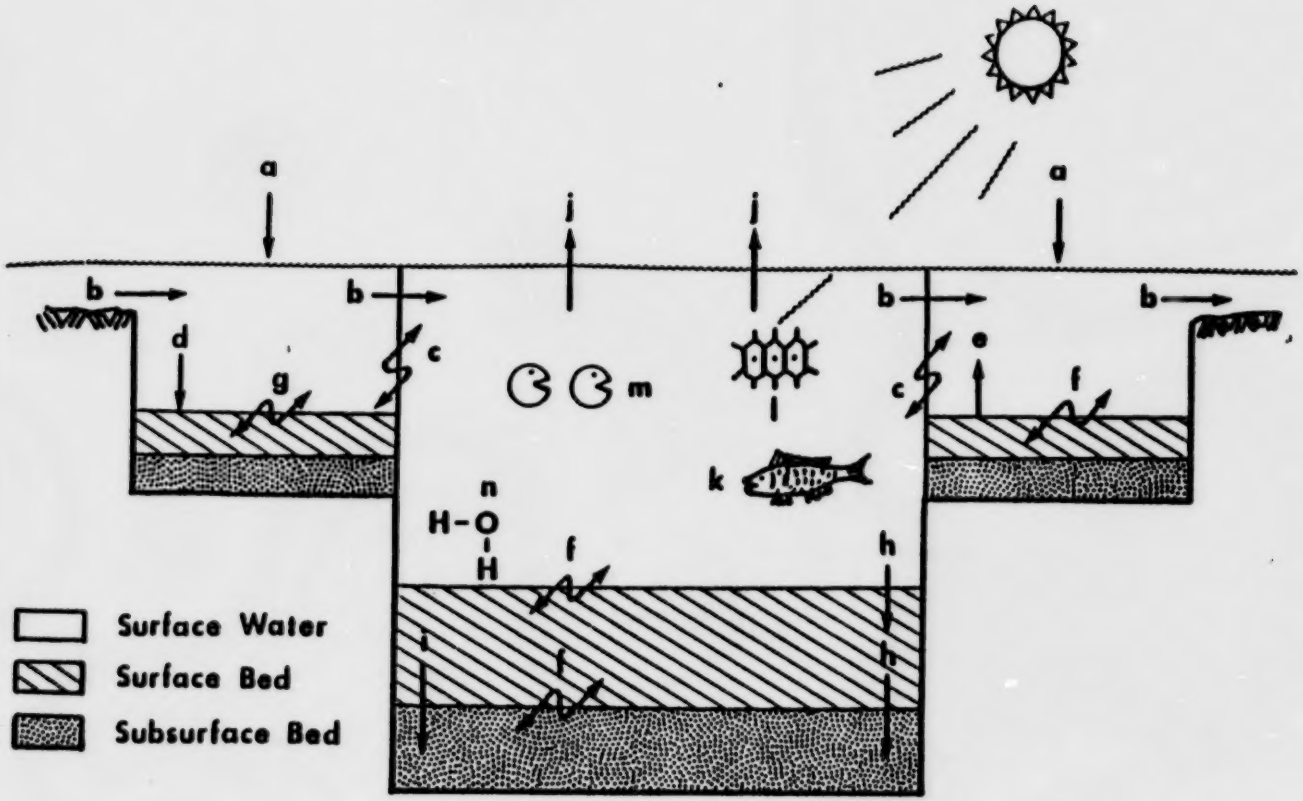


FIG. 2.4 Typical Transfer Processes in Exposure Models



(1) TRANSPORT PROCESSES

A) MASS LOADING
B) ADVECTION
C) DISPERSION
D) SETTLING
E) EROSION
F) PORE WATER DIFFUSION
G) SEDIMENT TURNOVER
H) PERCOLATION
I) SEDIMENTATION
J) VOLATILIZATION

(2) TRANSFORMATION PROCESSES

K) BIOCONCENTRATION
L) PHOTOLYSIS
M) BIODEGRADATION
N) HYDROLYSIS
O) REDUCTION - OXIDATION

FIG. 2.5 The Transport and Transformation Processes of TOXIWASP Model.

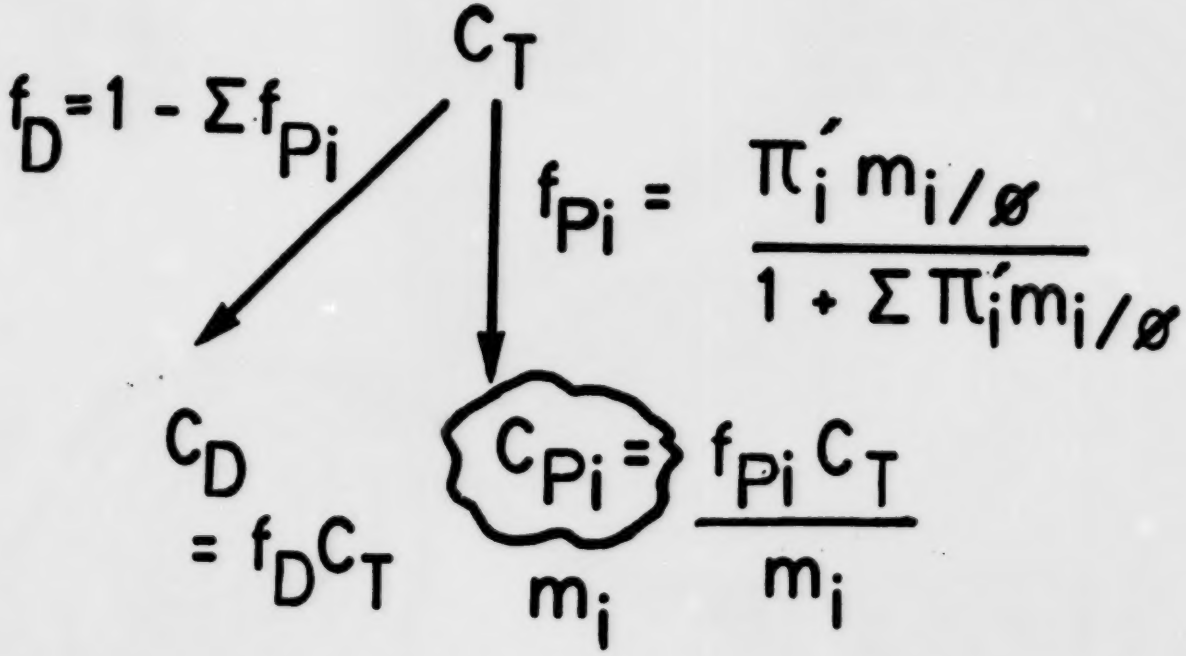
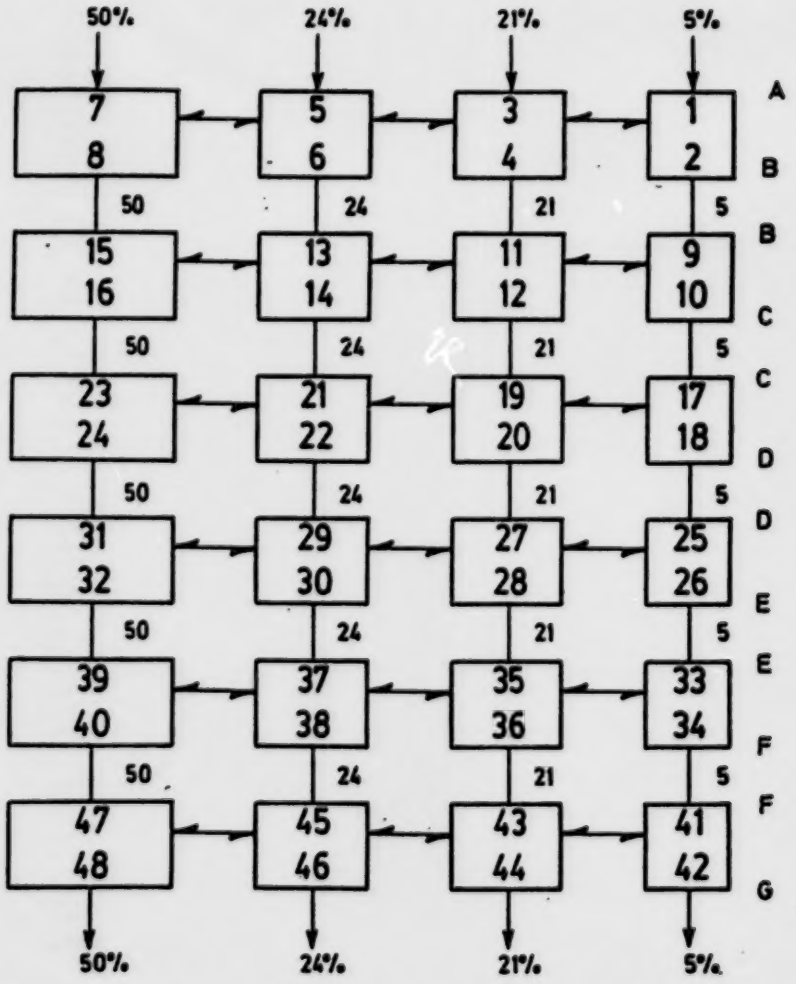
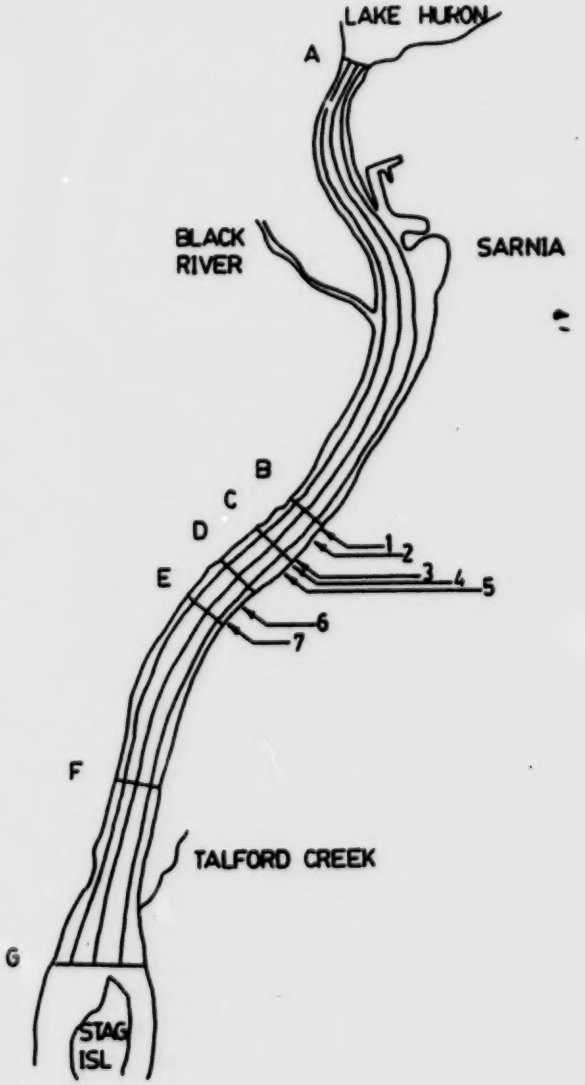


FIG. 2.6 The Partitioning Process in an Exposure Model

FIG. 2.7 A Typical Planwise Cell Discretization for TOXIWASP





Upper St. Clair River Model Segment Flow Pattern (all flows are percent of total flow).

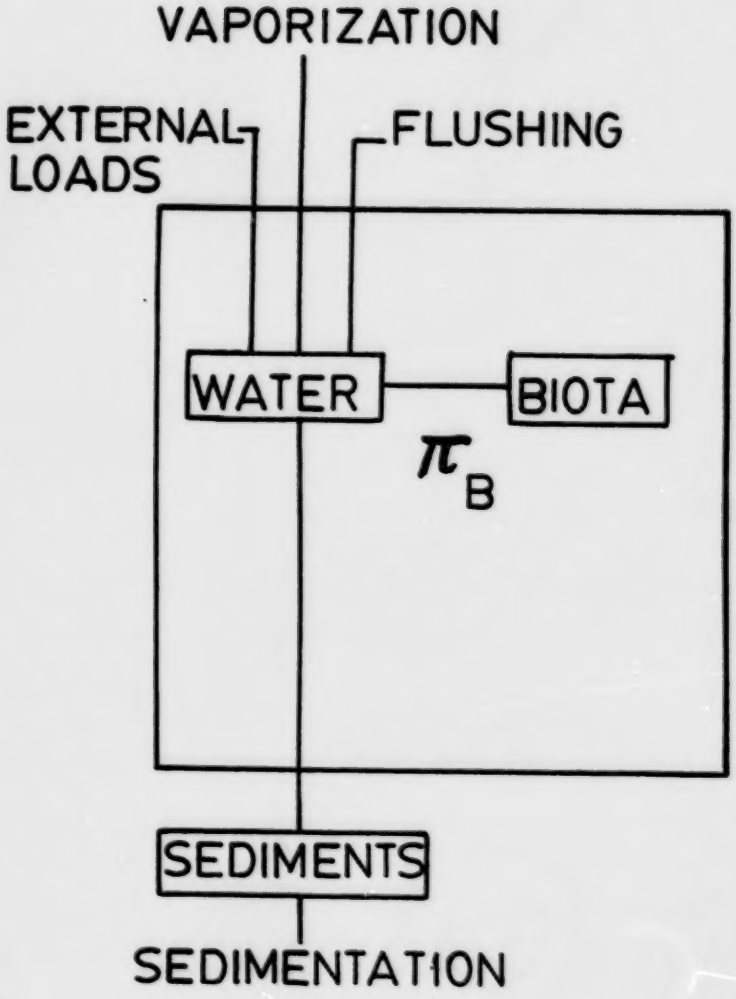


FIG. 2.8 THE WHITMORE (1977) MODEL (CHAPRA, 1983)

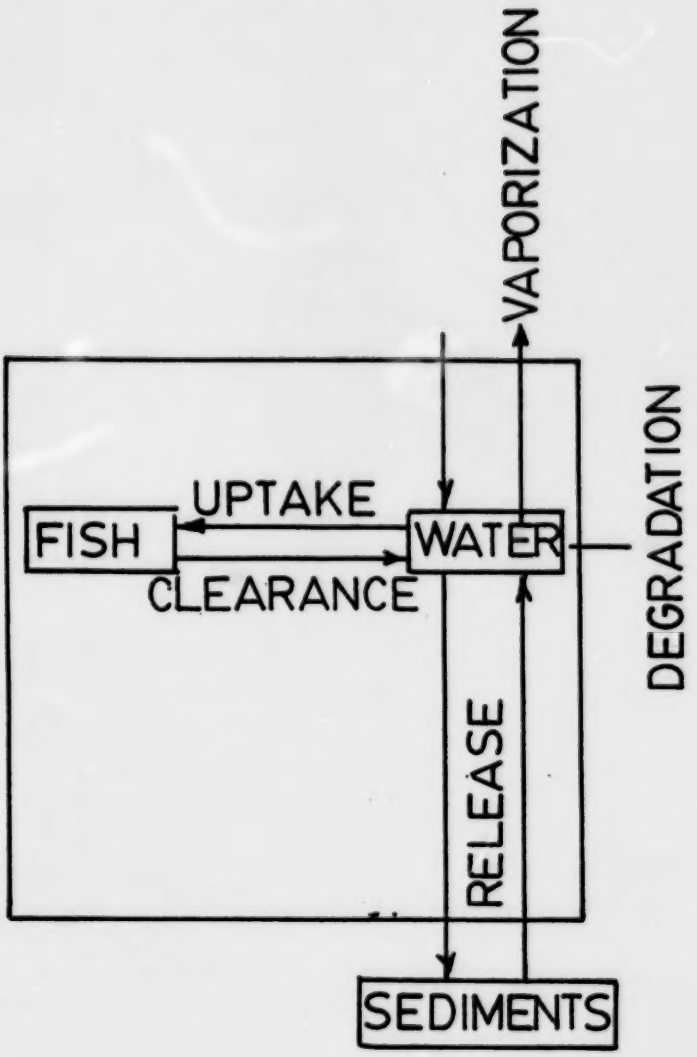


FIG. 2.9 The Needly Model (Chapra, 1983)

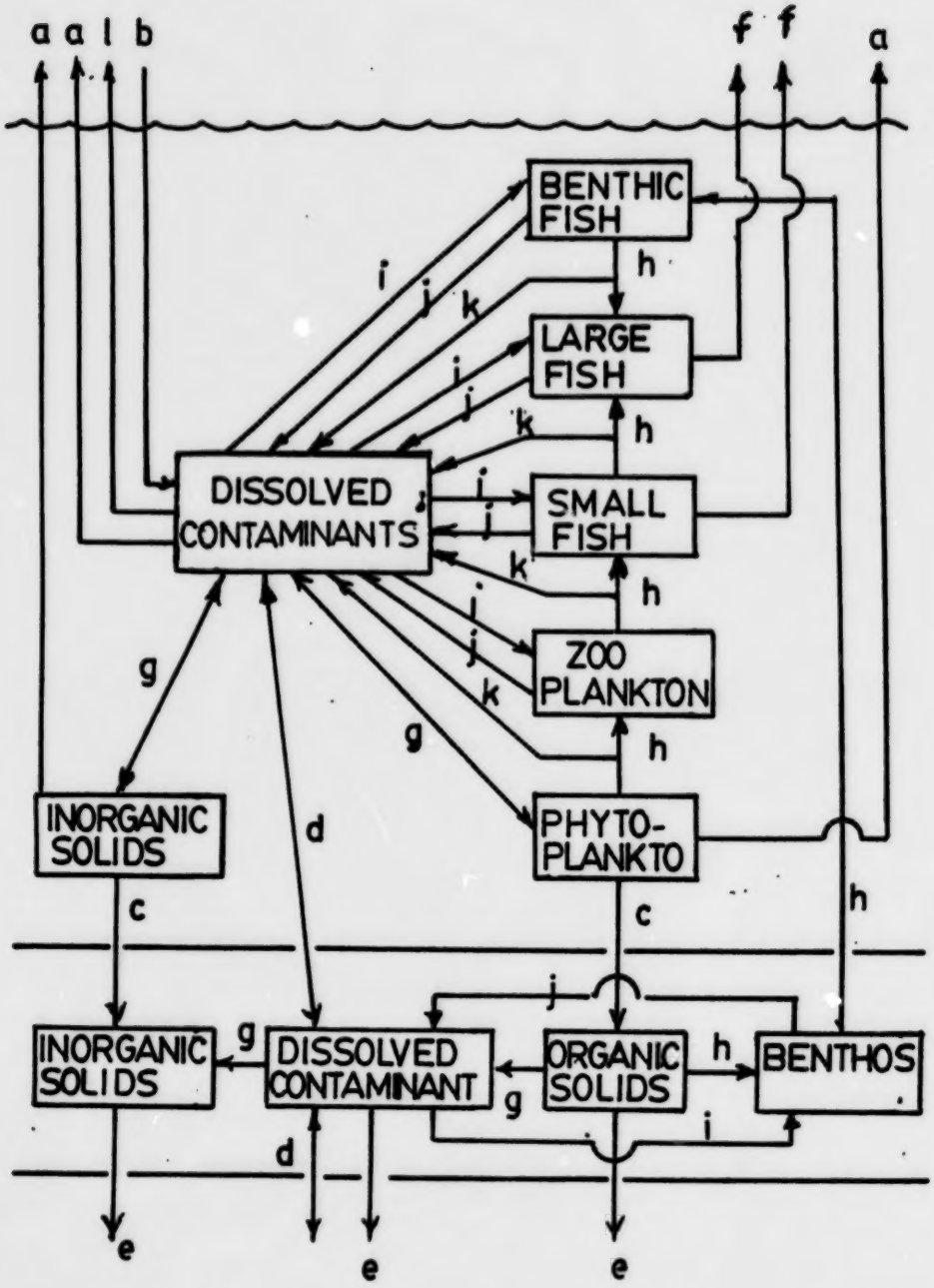


FIG. 2.10 The Chapra Model (1983)

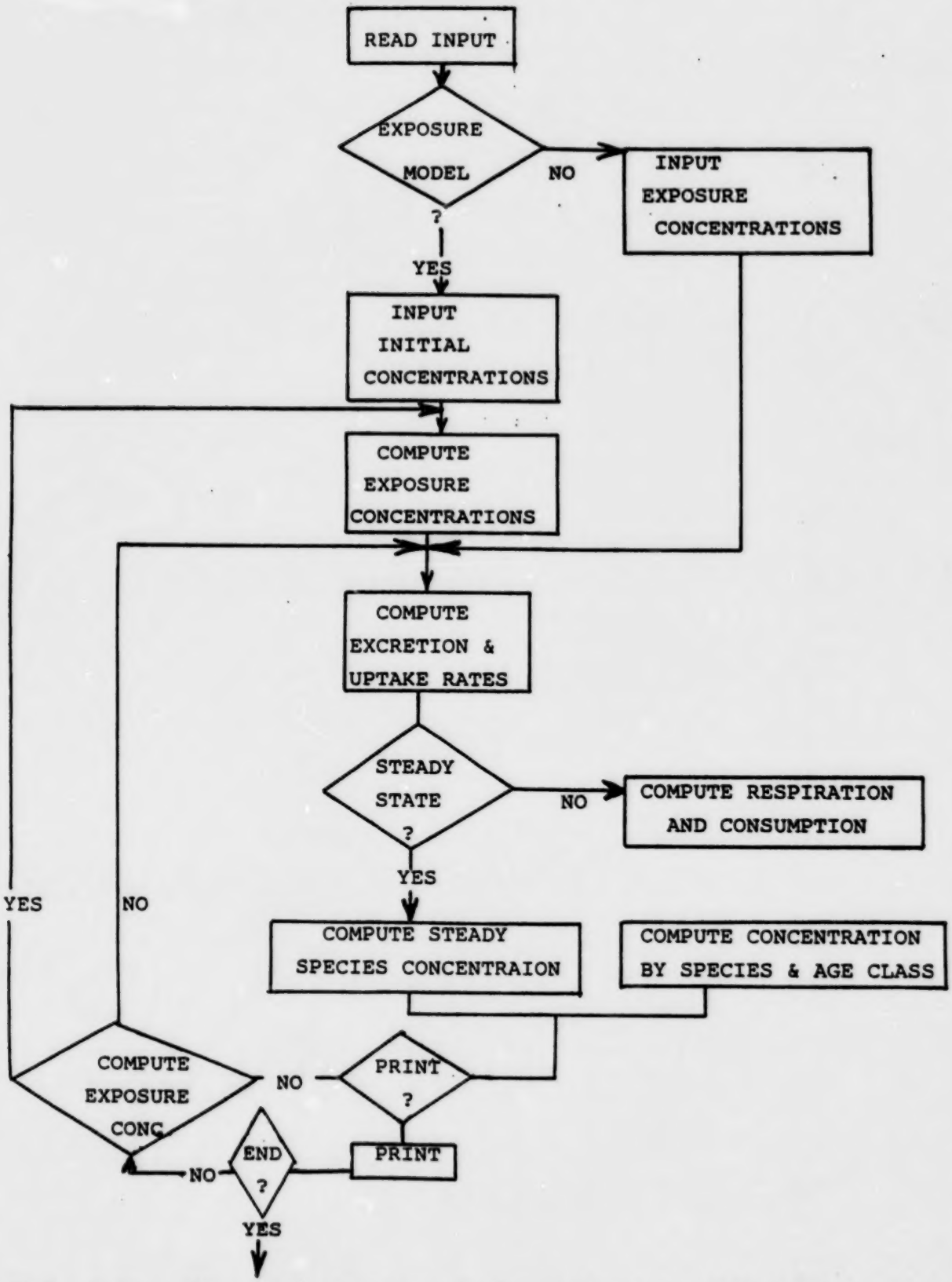


FIG. 2.11 The Manhattan College Model WASTOX (Connelly, 1986)

1 EXPOSURE CONCENTRATIONS
-DISSOLVED
-SORBED
2 FOOD WEB
PREDATOR - PREY
(BY AGE & SEASON)
3 CONSUMPTION,
4 ASSIMILATION
-FOOD
-TOXICS
5 GROWTH RATE
6 WET/DRY WEIGHT & LIPID CONTENT
7 EXCRETION
8 RESPIRATION
9 BCF
10 BAF
11 MOBILITY/MIGRATION/SPAWNING
12 HARVESTING/REMOVAL
13 DEATH & RECYCLING
14 BIOTURBATION
15 FEEDBACK TO EXPOSURE MODEL
16 METABOLISM

FIG. 2.12 Some Factors that Affect the Contaminant Uptake and Accumulation in Biota

CHAPTER 3

A BRIEF SUMMARY OF AN AQUATIC BIOACCUMULATION MODEL OF ORGANIC CHEMICALS

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INTRODUCTION

Background

The work described in this summary is part of an overall research project on the variability of chemicals in aquatic food chains (Thomann 1987a). The specific details of the relationship of food chain behavior and the log K_{ow} of organic chemicals is given in (Thomann 1987b).

The purpose of this summary is to provide a brief review of the basic structure of the food chain model, indicate the relationship to the octanol water partition coefficient and draw some general conclusions regarding the need for and use of food chain modeling in water quality monitoring and allocation activities.

There has been a considerable amount of discussion in recent years about the actual occurrence of food chain accumulation. That is, a simple lipid partitioning of the chemical into the lipid pools of aquatic organisms has been used to determine the concentration of the chemical. This simple bio-concentration calculation has been widely used in the United States in establishing water quality criteria for organic chemicals.

In this view, the aquatic system is seen as a series of "lipid packets" that sorb the organic chemical directly from the water. Food chain effects are non-existent in this model since there is no apparent mechanism for chemicals to accumulate from one level of the food chain to the next. The procedure is then very simple. All one needs to know is the octanol water partition coefficient (K_{ow}) and the available chemical concentration in the water. The concentration in the aquatic organism is then simply given by

$$\nu = c\ K_{ow}\ p \qquad (1)$$

where

ν = organism chemical concentration (μg/g(w))

c = chemical concentration in the water (μg/L)

K_{ow} = the octanol water partition coefficient, and

p = lipid fraction of organism (kg(lip)/kg(w)).

The difficulty with this simple procedure is that there is some considerable growing evidence that for certain organic chemicals, there is an apparent significant increase of the chemical concentration in the organism above that which would be expected from uptake from the water only.

Since there are data that indicate some significant bioaccumulation in the food chain, it is necessary to construct modeling frameworks that incorporate the principal features of chemical uptake and food chain transfer. A model framework for this purpose is discussed in the next section.

THE FOOD CHAIN MODEL

Generic Versus Site Specific Food Chains

There are two approaches to structuring a food chain model, each with differing purposes and objectives. The first is a generic approach where generalized relationships are applied to a simple "one-dimensional" food chain. That is, a single predator feeds on a single prey. This generic type structure is useful for general screening analyses of chemicals and general behaviour of chemicals in abstract but very easily understood food chains. This is the modeling focus presented in this paper.

The second approach is to construct a food chain model that is fully site specific. The food web is described as completely as

possible, using for example, analyses of food contents to infer feeding patterns. Organism specific growth rates are used, associated food assimilation efficiencies are assigned and any specific migratory behavior is explicitly included (Thomann et al. 1984, Connolly et al. 1985). This approach is most useful for describing the particular behavior of an individual food chain for use in detailed water quality analyses and determination of site specific waste load allocations.

Equations for Generic Food Chain-Water Uptake Only

Considering a simple food chain of four levels with level #1 as the base of the food chain represented by the phytoplankton. Then a mass balance of a chemical around a defined food chain compartment is given by (Thomann 1987)

$$\frac{d\nu'_i}{dt} = k'_{ui}\, w_i\, c + \alpha_{i,i-1}\, C'_{i,i-1}\, w_i \frac{\nu'_{i-1}}{w_{i-1}} - K_i \nu'_i \qquad (2)$$

where

ν'_i = chemical whole body burden (μg/organism) of the predator

k'_{ui} = uptake rate of the chemical from the water (L/d-kg(w) kg(w) = kg wet wt)

w = wet weight of organism (kg(w))

$\alpha_{i,i-1}$ = chemical assimilation efficiency (μg absorbed/μg ingested)

$C'_{i,i-1}$ = specific consumption rate (kg(w) prey/kg(w) predator-d)

ν'_{i-1} = chemical body burden of prey (μg/organism), and

K = chemical excretion rate, d^{-1}

Since

$$\nu' = \nu w_{lip} \qquad (3)$$

where w_{lip} = organism weight on a lipid basis (μg lipid), Eq. (2) can therefore be written using a lipid based concentration of the chemical in the organism as follows

$$\frac{d\nu_i}{dt} = k_{ui}c + \alpha_{i,i-1} C_{i,i-1} \nu_{i-1} - (K_i + G_i) \nu_i \quad (4)$$

where now all concentration and parameters (uptake and food consumption rates) are expressed on a lipid basis. Also, G = the net growth rate of the organism and is given by

$$G = aC - r \quad (5)$$

where r is the organism respiration rate (d^{-1}) and a is the food assimilation efficiency. Equation (5) results from a simple growth equation on the weight of the organism given by

$$\frac{dw}{dt} = (aC - r)\, w = Gw \quad (6)$$

The food consumption rate is then estimated from Eq. (5) as

$$C = \frac{G + r}{a} \quad (7)$$

1. **Uptake From Water, Variable Efficiency.** – The uptake rate in the above equations, k_{ui} represents the volumetric rate at which the chemical is transferred across the gill membrane of fish, for example. Measurements of the efficiency of transfer across the lipo-protein membranes of fish have been made (see, for example, (McKim et al. 1985)). In general, these laboratory data indicate a reduced transfer efficiency at low K_{ow} values (< 5), increasing efficiency values at intermediate levels of the octanol water partition coefficient and then declining values of efficiency at higher K_{ow} levels of greater than about 7.

Recognizing that the uptake rate is directly related to the respiration rate of the organism and the efficiency of transfer, Thomann (1987a) indicates that an approximate relationship for the uptake rate as a function of the efficiency of transfer is given by

$$k_u \sim 1000 \frac{w^{-0.2}}{p} E\ (K_{ow}) \qquad (8)$$

where E (K_{ow}) is the efficiency of transfer as a function of the octanol water partition coefficient. This functional relationship is non-linear as noted previously and to first approximation for larger organisms of weight greater than about 100 g(w) is given by the following equations.

For log K_{ow} = 2-3:

$$\log E = -1.5 + 0.4 \log K_{ow} \qquad (9a)$$

For log K_{ow} = 3 - 6:

$$E = 0.5 \qquad (9b)$$

For log K_{ow} 6 - 10:

$$\log E = 1.2 - 0.25 \log K_{ow} \qquad (9c)$$

These equations represent an empirical relationship between observed efficiencies and the octanol water partition coefficient. As such, a full mechanistic explanation for the behavior as given by these equations requires more detailed study. However, the basic rationale is that at lower K_{ow} values, the transfer across the membrane is rapid through aqueous diffusion layers, but is hindered by the lipid membrane because of low fat solubility. At increasing octanol water partition coefficient levels, the resistance form the membrane is reduced and the transport is proportional to K_{ow}. At very high K_{ow} values, water solubility of the chemical limits transport and the efficiency decreases.

The Field BCF

Using the above expressions for the uptake rate and assuming that at equilibrium, the lipid based bioconcentration factor (BCF) is equal to the octanol water partition coefficient, the excretion rate can be calculated as a function of the K_{ow}. Under field conditions, however, the growth of the organism must be recognized. That is, in Eq. (4), the relevant "loss

mechanism" is the quantity K + G. It can then be shown under field generic growth conditions using

$G = 0.01\ w^{-0.2}$

as representative of the growth rate, that the field BCF (N_w) is approximately

$$N_W = K_{ow} \{ 1 + \frac{10^{-6} K_{ow}}{E\ (K_{ow})} \} \qquad (11)$$

Figure 3.1 from (2) shows that the calculated field log BCF reaches a maximum of 5.5 at a log K_{ow} of about 6. At higher log K_{ow} values, the field BCF decreases due to decreased efficiency of transfer and increasing effect of organism growth.

The implication from Fig. 3.1 is that if comparisons are to be made between field observed concentration factors and the octanol water partition coefficient to determine the degree of bioaccumulation, if any, then the comparisons should be made to the estimate field BCF with the growth rate of the organism included.

When this comparison was made for the field observed concentration of PCB in the lake trout of Lake Michigan, it was found that the observed concentration was about one order of magnitude higher than the concentration that would have occurred if only uptake from the water were considered (see Thomann, 1987b for further details).

Phytoplankton BCF

The above discussion applies to the upper trophic levels of the food chain. The laboratory BCF for the base of the food chain, the phytoplankton, have been compiled (Thomann 1987b) and are shown in Fig. 3.2. It appears from these data that the phytoplankton BCF is approximately equal to the octanol water partition coefficient. There are some indications that the BCF is a constant at log K_{ow} values above about

6. Both relationships are shown in Fig. 3.2. The food chain calculations summarized below are particularly sensitive to the BCF of the phytoplankton.

Generic Food Chain Model - Bioaccumulation

The additional chemical input due to consumption of contaminated prey as shown in Eq. (2) can now be included. A steady state generic framework is used where the use of "steady state" in food chain compartment models has previously been discussed (Thomann 1981).

Steady State Equations for Field BAF

The following set of equations can be derived under steady state and using a generic four level food chain structure:

$$N_{w1} = \nu_1 c \tag{12a}$$

$$N_2 = N_{w2} + f_{21} N_{w1} \tag{12b}$$

$$N_3 = N_{w3} + f_{32} N_{w2} + f_{32} f_{21} N_{w1} \tag{12c}$$

$$N_4 = N_{w4} + f_{43} N_{w3} + f_{43} f_{32} N_{w2} + f_{43} f_{32} f_{32} f_{21} N_{w1} \tag{12d}$$

where

$$f_{i,i-1} = \frac{\alpha_{i,i-1} C_{i,i-1}}{K_i + G_i} \tag{12e}$$

In Eqs. (12), N_{wi} represents the field BCF of the ith level of the food chain, i.e.

$$N_{wi} = \frac{k_{ui}}{K + G} \tag{13}$$

The cumulative effect of the transfer of chemical from the lower levels of the food chain to the top predator level can be seen. Also the significance of the phytoplankton BCF, N_{wi} can be seen.

The only remaining parameter to be specified is the chemical assimilation efficiency, α. This parameter has been measured in the laboratory for some chemicals and some organisms. However, additional effort to obtain measurements of the chemical food assimilation efficiency

is necessary especially over a broad range of octanol partition coefficients and food and organism types.

On the grounds that the mechanism of the assimilation of the chemical through ingestion of food is similar to the transfer of the chemical across the gill membrane, to first approximation it is assumed that the relationship between the assimilation efficiency with log K_{ow} is given by Eqs. (9).

Comparison to Field Data

A determination can be made about the adequacy of the model given in Eqs. (12) by assigning some generic measures of growth, respiration (and resulting food consumption rates) and approximate average weights of each trophic level. For simplicity, the fraction lipid and the food assimilation efficiency were constant across the food chain at 0.1 and 0.8, respectively. The average weights for each level of the food chain were 0.1, 10, and 1000 g(w) for levels #2, 3, and 4, respectively.

The BAF for level #4, the top predator is compared to observed BAF data in Fig. 3.3. The data are largely from the Great Lakes and in some cases required assignment of % lipid or the fraction of the water column concentration in dissolved form.

The model calculations indicate that for level #4, the BAF reaches a maximum of more than one order of magnitude higher than the calculated field BCF with growth included. For a simple no-growth lipid partitioning, the field BAF is about one order of magnitude higher at a log K_{ow} of about 6.5.

To first approximation, then, the generic food chain calculation indicates that biomagnification is significant only in the region of log K_{ow} between about 5-7. Below log K_{ow} of about 5, the intake of chemical

from water and food is balanced by the loss of chemical due to excretion and growth. Above this level however, the excretion rate declines and at steady state a net accumulation of chemical occurs which results in concentrations above the expected level due to uptake from water only. Above log K_{ow} of about 7, the calculation indicates that the BAF levels off and then declines due to decreased efficiency of transfer across the membranes of the organism. The model results however, shown in Fig. 3 are sensitive to the choice of parameters, specifically the growth rate of each trophic level and the BCF of the phytoplankton.

Sensitivity to Phytoplankton BCF

The sensitivity of the top level BAF to two estimates of the phytoplankton BCF as shown in Fig. 3.2 is shown in Fig. 3.4. As indicated, the effect of the constant phytoplankton BCF is to more rapidly reduce the BAF at high K_{ow} to the calculated field BCF. The effect is negligible for log K_{ow} of < 6. Therefore, if the phytoplankton BCF is constant, the BAF for the top level of the food chain at high octanol partition coefficients would not refelect as substantial a food chain accumulation as with the phytoplankton BCF equal to the K_{ow}.

CONCLUSIONS

This summary of a food chain model using a generic food chain structure indicates that:

1. For organic chemicals with log K_{ow} of less than about 5, and for chemical screening purposes, complicated food chain modeling is not necessary. Rather, a simple lipid partitioning calculation using the K_{ow} as a surrogate for the partition coefficient is sufficient. Food chain biomagnification effects are apparently not significant in this region because of relatively high

excretion and growth rates and reduced transfer efficiencies.

2. For organic chemicals with log K_{ow} in the range from about 5–7 food chain magnification may be significant. The degree of biomagnification depends on the organism growth rate, the phytoplankton BCF and the chemical assimilation efficiency as well as other factors.

   The biomagnification in this region is about one order of magnitude higher than would be calculated form simple lipid partitioning. Therefore, for this group of organic chemicals, almost all of the chemical concentration in the upper levels of the food chain would be due to consumption of contaminated food rather that uptake from the water.

   Also, for this region of log K_{ow}, a food chain model structure is necessary. The degree of complexity of the model may vary from a simple steady state generic framework, such as discussed in this summary or a more complicated site specific time variable, age dependent model.

3. Above log K_{ow} of about 7, model calculations indicate that there is some reason to believe that the field BAF will not continue to increase. A plateau and subsequent decline in BAF with increasing log K_{ow} may occur due to decreased transfer efficiency of the chemical and growth effects. This region of the model however does not have any field data for confirmation and as such the model results represent a projection of expected BAF values.

REFERENCES

Thomann, R.V., (1987a). "Statistical Model of Environmental Contaminants Using Variance Spectrum Analysis", National Science Foundation Final Report, 161 p. + Appendix.

Thomann, R.V., (1987b). "Bioaccumulation Model of Organic Chemicals in Aquatic Food Chains", Submitted for publication.

Thomann, R.V. and Connolly, J.P., (1984). "Age Dependent Food Chain Model of PCB in Lake Michigan Lake Trout", Env. Sci. & Tech. Feb. 1984.

Connolly, J.P. and Tonelli, R., (1985). "Modeling Kepone in the Striped Bass Food Chain of the James River Estuary", Est., Coastal and Shelf Sci., 20, 349–366.

McKim, J., Schmieder, P., and Veith, G., (1985). Tox. Appl. Pharm., 77:1–10.

Thomann, R.V., (1981). Can. J. Fish. Aquat. Sci., 38:280–296.

FIGURE CAPTIONS

Fig. 3.1. Comparison of hypothesized field BCF (Eq. 11) for organism weight > 10–100 g(w) to simple lipid partition (growth rate = 0). Uptake efficiency from Eq. (9), p = 0.10.

Fig. 3.2. Phytoplankton BCF (see [2] for references of data).

Fig. 3.3. Comparison of calculated BAF as function of K_{ow} to data (from [2], see that reference for data citations).

Fig. 3.4. Sensitivity of BAF for level #4 to phytoplankton BCF (see [2] for references of data).

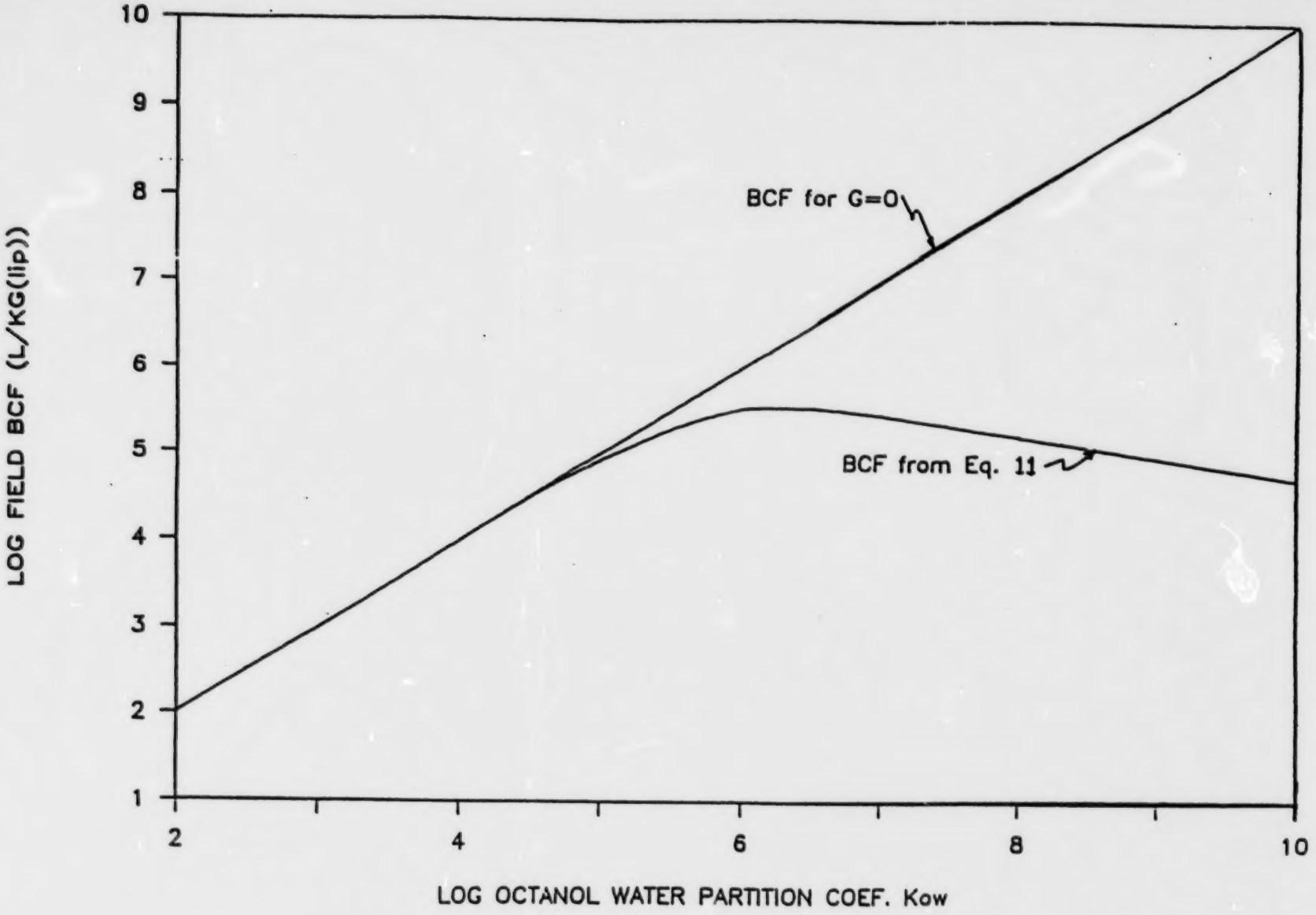

Figure 3.1 Comparison of hypothesized field BCF (Eq. 11) for organism weight > 10-100 g(w) to simple lipid partition (growth rate = 0). Uptake efficiency from Eq. (9), p = 0.10.

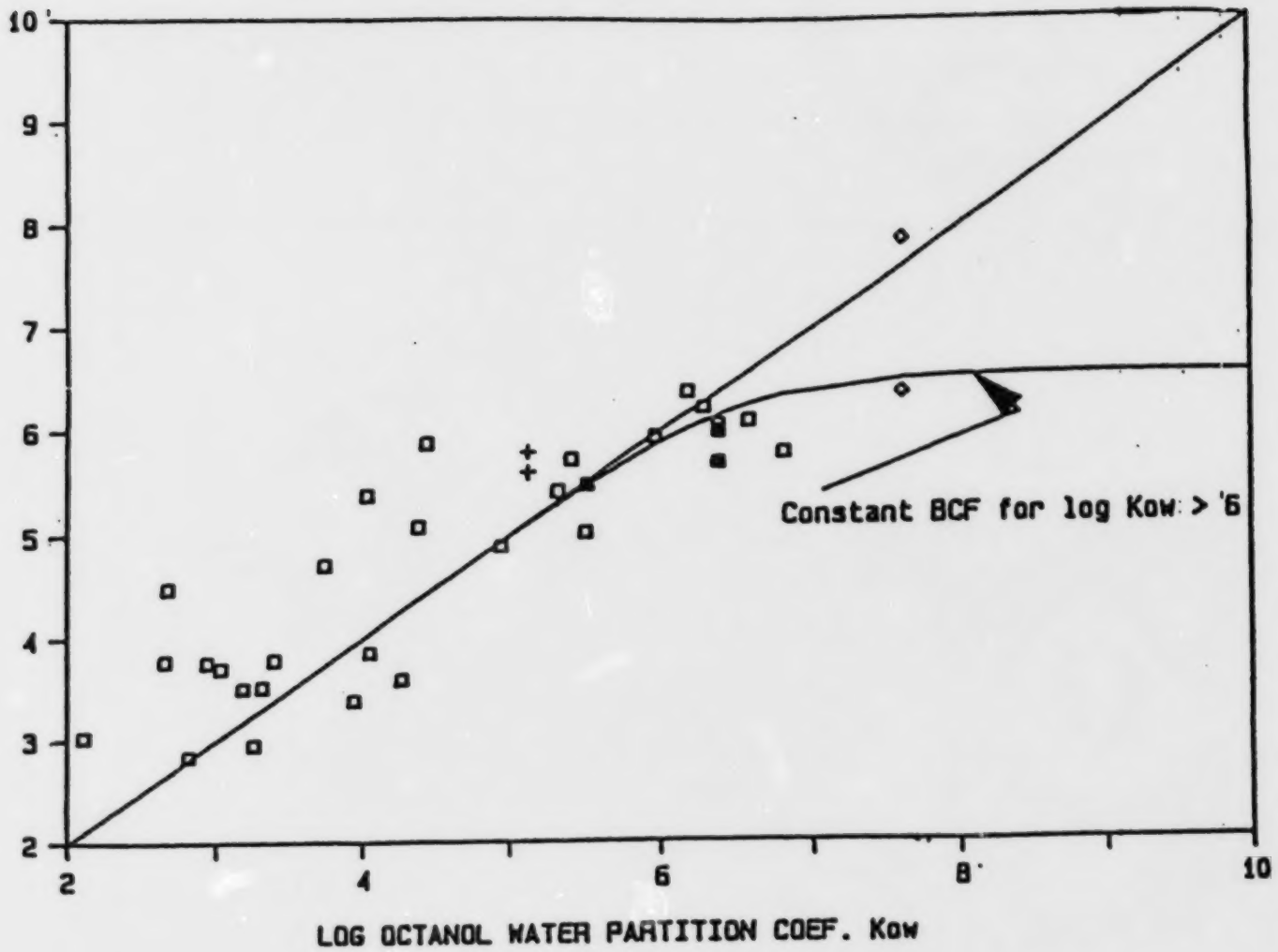

Figure 3.2 Phytoplankton BCF (see[2] for references of data)

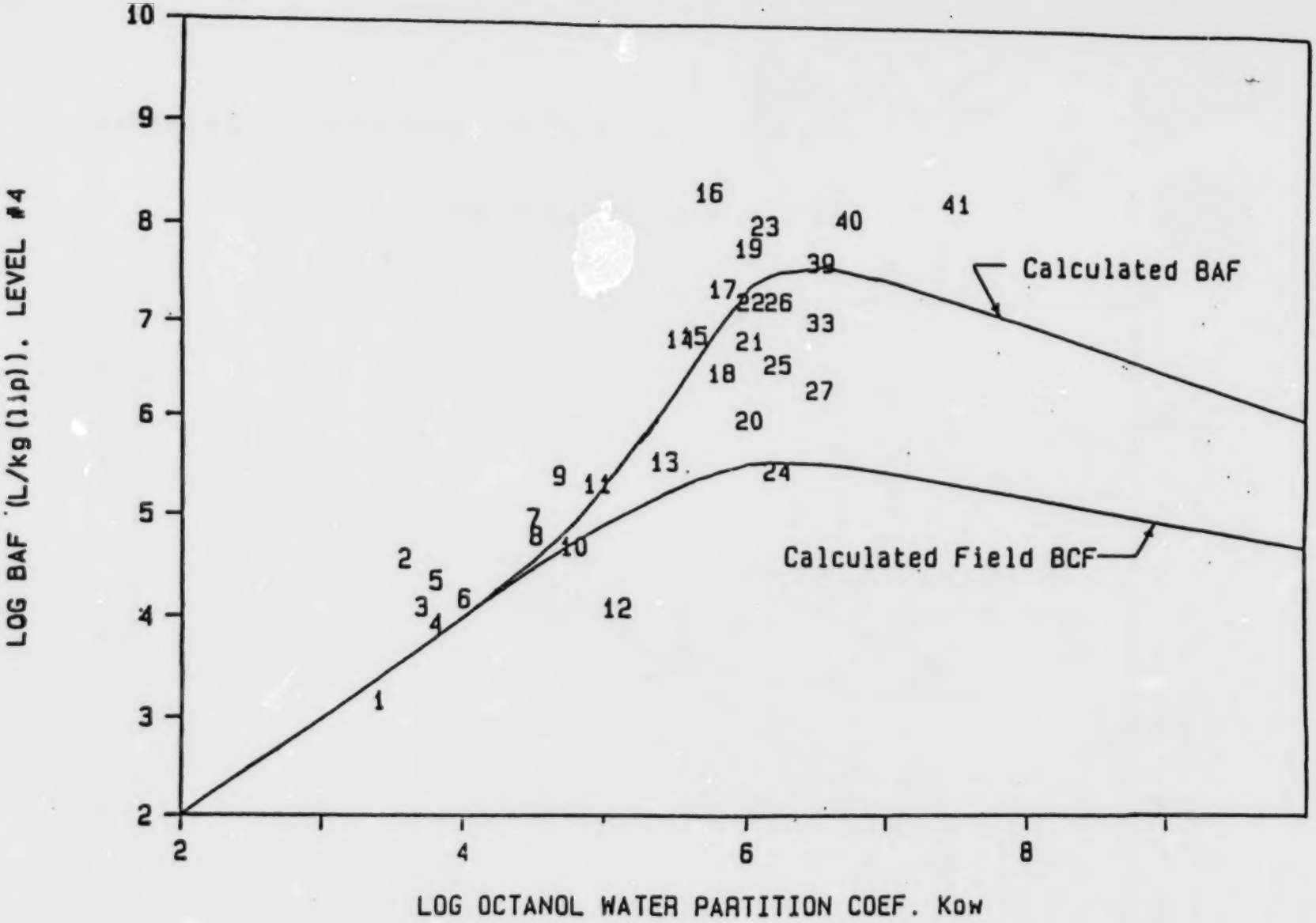

Figure 3.3 Comparison of calculated BAF as function of K_{ow} to data (from [2], see that reference for data citations).

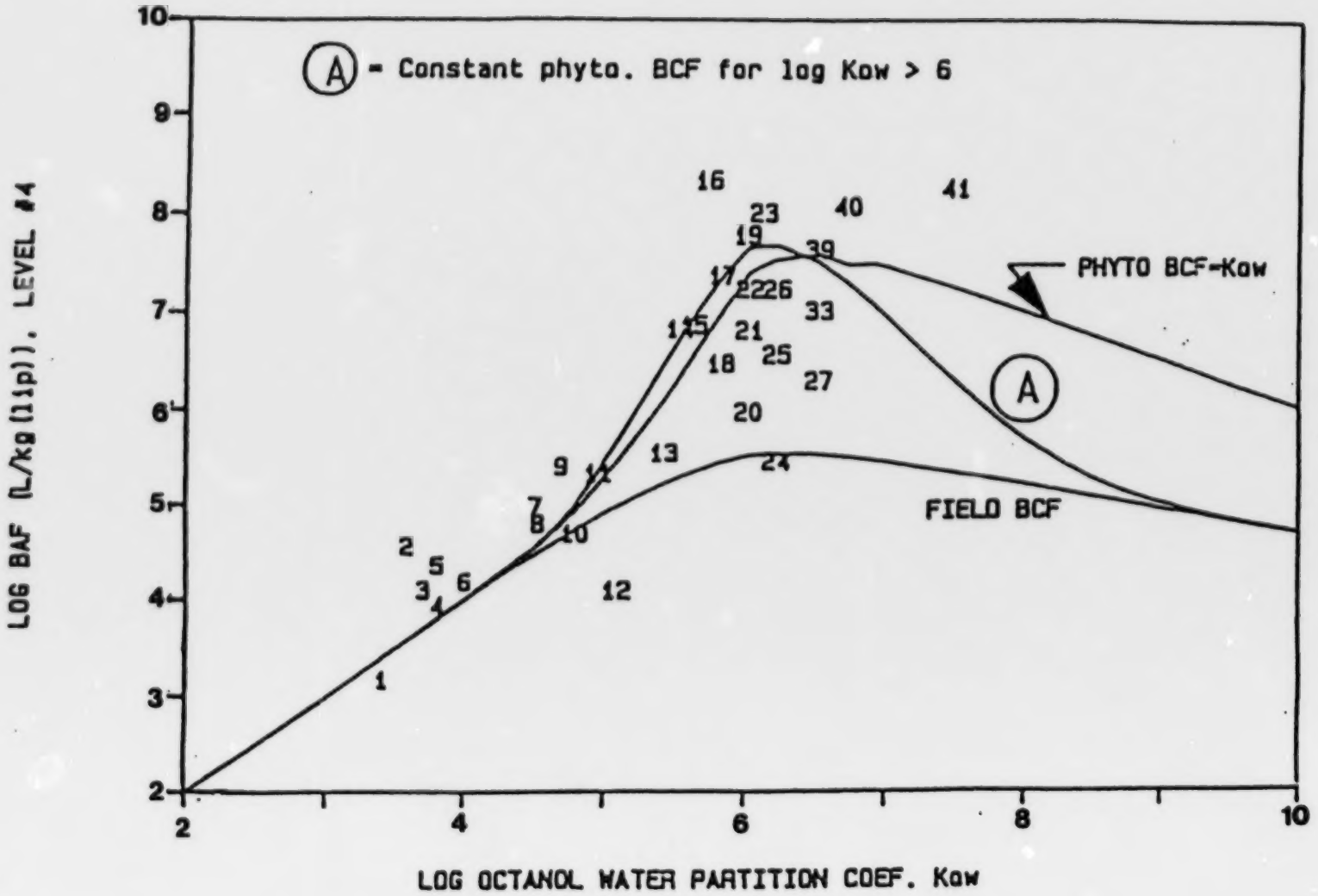

Figure 3.4 Sensitivity of BAF for level #4 to phytoplankton BCF. (see [2] for references of data)

CHAPTER 4

FACTORS DETERMINING THE UPTAKE AND FOOD CHAIN TRANSFER OF HYDROPHOBIC ORGANIC CHEMICALS IN FISH

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ABSTRACT: Correlations between the bioaccumulation tendency of organic chemicals in aquatic organisms and 1-octanol-water partition coefficients are generally satisfactory for moderately hydrophobic chemicals (log K_{ow} < 5), but show a loss of linearity for very hydrophobic compounds (log K_{ow} > 5) in both laboratory experiments and under field conditions. In order to establish the possible cause(s) of this phenomenon the roles of metabolism, exposure time, membrane permeation, lipid solubility, bioavailability, fish growth, chemical uptake from food and elimination to the faeces on the bioconcentration potential of chemicals and their relative importance are discussed. The role of food chain accumulation or biomagnification is discussed and it is concluded that at each trophic level of the food chain a chemical's concentration or fugacity increases by a factor of 3 to 5.

INTRODUCTION

The ability of organic chemicals to bioaccumulate and elicit a certain toxic response in aquatic organisms is usually ascribed to the partitioning tendency of these chemicals between water and the organism or a particular target site within the organism. Since partitioning of organic chemicals is predominantly into the lipid tissue of the organism, and 1-octanol resembles these lipids in many respects, various types of activities, toxicities and bioaccumulation phenomena have been successfully correlated with the 1-octanol-water partition coefficient, K_{ow}. For example linear correlations with respect to K_{ow} have been observed for narcotic action of drugs (Mullins 1954), for acute toxicities in fish and crustaceans (Bobra et al. 1985, Veith et al. 1983, Hermens et al. 1985, Abernethy and Mackay 1987) and for bioconcentration factors of organic environmental contaminants in fish (Neely et al. 1974, Mackay 1982, Opperhuizen et al. 1985). Further, transport parameters such as kinetic rate constants for uptake and elimination in fish can be related to K_{ow} (Gobas et al. 1986a, Mackay and Hughes 1984, Gobas and Mackay 1986). However, when K_{ow} becomes relatively high, a loss of the linear

correlation is usually observed (Dearden 1985). In laboratory experiments observed bioconcentration factors of high K_{ow} chemicals (i.e., log K_{ow} > 5) are usually lower than predicted from the K_{ow} (Bruggeman 1984, Opperhuizen et al. 1985). However, bioconcentration factors of the same chemicals in the field, such as in Lake Ontario (Oliver and Niimi 1985), are often higher than predicted from K_{ow}. This severely limits the predictive ability of the presently used linear relationships between the BCF and the 1-octanol-water partition coefficient and causes uncertainty about the actual mechanisms involved. To the class of chemicals with log K_{ow} exceeding 5 belong many persistent contaminants of environmental concern such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs), some of which have been observed to be extremely toxic to mammals and aquatic organisms (Safe 1984).

The objective of this paper is to address and investigate some of the factors that singly or in combination may cause the apparent loss of linear correlation between bioconcentration factors in fish and K_{ow}. These are exposure time, metabolism, bioavailability, membrane permeation and lipid-water partitioning. We also discuss briefly the role of food uptake and food chain accumulation (or biomagnification). First, it is useful to review the mathematical background of presently used bioconcentration models.

BIOCONCENTRATION IN FISH

Bioconcentration is the process by which fish or other aquatic organisms absorb chemicals only from the water. Bioconcentration does therefore not include chemical uptake from food i.e. biomagnification,

which we discuss later.

Since hydrophobic organic chemicals have a relatively low affinity for water compared to the fish lipids, a fish when exposed to contaminated water absorbs chemicals from the water until the chemical's fungacities in water (f_w) and fish (f_F) are equal i.e. the ratio of chemical's concentrations in the fish C_F, and water, C_w reaches the fish/water partition coefficient, K_C (Mackay 1982).

As has been discussed in more detail elsewhere the fugacity f can be viewed as the chemical's "escaping tendency" from a phase; it is linearly related to concentration C through a fungacity capacity Z, i.e. C equals $Z \cdot f$ (Mackay and Paterson 1982). When the water and fish have reached equilibrium and by definition their fugacities are equal, the fish/water partition coefficient or bioconcentration factor K_C is C_F/C_w or Z_F/Z_w. For many organic chemicals a simple two compartment (i.e. fish/water) model following first order kinetics gives a kinetic description of the bioconcentration process. The expression for fish/water exchange assuming no variation of the fish volume with time (e.g. no growth) is then given by:

$$V_F \cdot Z_F \cdot df_F/dt = V_L \cdot Z_L \cdot df_L/dt = D_F \cdot (f_W - f_L) \quad (1)$$

where the subscripts F, L and W refer to respectively the fish, the fish lipids and water, V is the volume (m^3) of the respective phases, t is time (h) and D_F is the fish/water transport parameter (mol/Pa.h), which is related to the more conventional uptake and elimination rate constants k_1 and k_2 according to:

$$k_1 = D_F/(V_F \cdot Z_W) \quad (2)$$

$$k_2 = D_f/(V_F \cdot Z_F) \quad (3)$$

Integration of Eq. (1) with a constant f_W and an initial f_F of zero

gives

$$f_F = f_W \cdot (1 - \exp(-D_F \cdot t/V_F \cdot Z_F)) \quad (4)$$

Since F_F is C_F/Z_F and f_W is C_W/Z_W Eq. (5) can be rewritten as:

$$C_F = C_W \cdot \frac{Z_F}{Z_W} \cdot (1 - \exp(- D_F \cdot t/V_F \cdot Z_F)) \quad (5)$$

Equation (5) is equivalent to the solution of the more traditional differential equation describing uptake and release in fish i.e.

$$\frac{dC_F}{dt} = k_1 \cdot C_W - k_2 \cdot C_F \quad (6)$$

which after integration gives:

$$C_F = C_W \cdot \frac{k_1}{k_2} \cdot (1 - \exp(- k_2 \cdot t)) \quad (7)$$

The bioconcentration factor, K_C, is defined as the ratio of chemical concentration in the fish and water at steady state (i.e. $t = \infty$) and thus according to Eqs. (5) and (7):

$$K_C = C_F/C_W = k_1/k_2 = Z_F/Z_W = L \cdot Z_L/Z_W = L \cdot C_L/C_W = L \cdot K_L \quad (8)$$

where L is the volumetric lipid content of the fish i.e. V_L/V_F.

CORRELATIONS BETWEEN K_{ow} AND K_C

Since the lipid tissue of the fish is the principal site for bioaccumulation and 1-octanol is often a satisfactory surrogate for lipids, linear correlations are usually observed between K_C and K_{ow}. The partition coefficients K_{ow} and K_C can be expressed in thermodynamic quantities as the ratio of molar volumes, v, of the respective phases and the chemical's activity coefficient y, defined on a Raoult's basis in the two phases:

$$K_{ow} = \frac{v_W \cdot y_W}{v_O \cdot y_O} \quad (9)$$

$$K_C = L \cdot \frac{v_W \cdot y_W}{v_L \cdot y_L} \quad (10)$$

The activity coefficient y expresses the chemical's affinity for a phase.

It is inversely related to the chemical's mole fraction solubility x (mol/mol) in that phase i.e. y is 1/x for liquid chemicals or y is F/x for solid chemicals, where F is the fugacity ratio or ratio of solid to liquid solubilities and x/F is the chemical's subcooled liquid solubility (Mackay and Shiu 1984).

From Eqs. (9) and (10) it follows that correlations between K_C and K_{ow} will be linear i.e. K_C/K_{ow} is constant as long as y_L/y_o remains constant.

For many chemicals, generally with log K_{ow} between 2 and 5, correlations between log K_C and log K_{ow} are usually linear. However, recent experimental data obtained by the authors and others (Opperhuizen et al. 1985 and 1986, Burggeman et al. 1984, Muir et al. 1985 and 1986, Gobas et al. 1986b) have clearly shown a loss of linear correlation for a number of compounds. This is illustrated in Fig. 4.1, where bioconcentration factors as listed in Table 4.1 of a series of compounds in guppies (Poecilia Reticulata) are plotted versus their experimentally determined K_{ow}. The following conclusions can be reached from Fig. 4.1:
(1) For compounds with log K_{ow}s between 2 and 5.5, log K_L and log K_{ow} show generally a linear correlation such as for the data in Table 4.1 (confidence intervals have a 95% probability):

$$\log K_L = 1.01\ (+/-\ 0.32) \cdot \log k_{ow} + 0.323\ (+/-\ 1.5)$$
$$n = 14,\ r^2 = 0.76 \qquad (11)$$

(2) Compounds with log K_{ow} higher than 6 have lower bioconcentration factors than expected based on Eq. (11). For these high K_{ow} compounds bioconcentration factors no longer increase with respect to K_{ow}, but show a maximum of log K_L of approximately 6 for compounds with log K_{ow}s of 5 then a gradual decrease with a further increase in K_{ow}.
(3) PCDDs have much lower BCFs than expected from their high K_{ow}s (Muir

1986, Opperhuizen et al. 1986, Gobas et al. 1986b). It is remarkable, however, that this does not seem to be the case for the congener 2, 3, 7, 8 TCDD, which has been observed to bioconcentrate in rainbow trout (K_C = 9270) (Branson et al. 1986).

(4) Other chlorinated and brominated compounds (Opperhuizen et al. 1985, Bruggeman et al. 1984, Zitko and Hutzinger 1976) and also some dyes (Anliker and Moser 1986) have been observed to have an extremely low or perhaps negligible bioconcentration potential.

EXPOSURE TIME

It has been shown by several authors that the time needed to reach equilibrium between the water and the fish increases with increasing K_{ow}. This is mainly the result of the longer half-life times $t_{1/2}$ i.e. $\ln 2/k_2$ for compounds with higher K_{ow}s due to an increased resistance to chemical transport in aqueous phases of the fish (Gobas et al. 1986a, Gobas and Mackay 1986). It is thus expected that super-hydrophobic compounds (log K_{ow} > 5 or 6), will require a very long time to reach equilibrium. BCFs measured in relatively short experiments (10–30 days) are found to be lower than they would be for prolonged experiments. As has been pointed out by Hawker and Connell (1985) a curvi-linear relationship between K_C and K_{ow} should therefore be expected. The experimental bioconcentration data (Fig. 4.1), however, clearly suggest a "parabolic" behaviour of K_L with respect to K_{ow} in guppies with a maximum bioconcentration factor for compounds with log K_{ow}s between 5 and 6. The exposure time effect should cause a leveling of the K_L - K_{ow} slope and not a maximum followed by a drop. It thus seems unlikely that a relatively short exposure time alone can explain the observed bioconcentration behaviour of the high K_{ow} compounds.

The dependence of $t_{1/2}$ on K_{ow} can be estimated and thus taken into account by conducting experiments with compounds of variable K_{ow} and fitting the data to an expression of the type

$$t_{1/2} = A \cdot K_{ow} + B \qquad (12)$$

where A and B are constants (Mackay and Hughes 1984). The parameters A and B are fish-specific and are related to the fish size such that smaller fishes have shorter half times (Gobas and Mackay 1986). Conducting experiments with small fish such as guppies (average weight 0.2 - 0.5 g) thus eliminates the primary cause of the low bioconcentration due to short exposure times.

METABOLIC TRANSFORMATION

Metabolism clearly reduces the BCFs of compounds by enhancing the depuration rates with respect to the uptake rate. This can be shown by extending the fish-water two compartment model to include metabolic transformation, represented by the transformation parameter D_R and the first order metabolic rate constants k_R:

$$V_F \cdot df_F/dt = D_F \cdot (f_W - f_F) - D_R \cdot f_F \qquad (13)$$

Upon integration this equation becomes

$$C_F = C_W \cdot \frac{Z_F}{Z_W} \cdot \frac{D_F}{D_F + D_R} \cdot (1 - \exp\left(-\frac{D_F + D_R}{V_F \cdot Z_F} \cdot t\right)) \qquad (14)$$

Equation (14) shows that at steady state or infinite time the BCF i.e. the ratio of chemical concentrations in fish and water is no longer controlled solely by the thermodynamic quantities Z_F and Z_W but also by the relative rates of uptake, elimination and metabolic transformation. For example, it can be observed from Table 4.2 that some compounds have bioconcentration factors $K_{C,exp}$ which are lower than expected from their high K_{ow}s according to equilibrium relationship that K_C equals to $0.048 \cdot K_{ow}$ (Mackay 1982). This is due to an increase in the total

depuration constant ($k_R + k_2$) over the expected elimination constant k_2 (i.e. $k_1 \cdot K_{C,exp}$), which can be fully accounted for by the actually measured biotransformation rate constant k_R. The correlated biotransformation rate constant, $k_{R,cor}$ (i.e. $k_1 \cdot (1/K_{C,exp} - 1/K_{C,cor})$) is in agreement with the observed biotransformation rate constant, suggesting that indeed biotransformation is the cause for the low biotransformation factors of these compounds.

Most of the information that exists about the bioaccumulation behaviour of super-hydrophobic compounds comes from bioaccumulation experiments performed with poly-halogenated aromatic compounds such as PCBs, PBBs, PCDDs and mirex. Present experience of transformation rates of organic chemicals in organisms, and in the environment in general, indicates that halogenated aromatics have extremely low biotransformation rates. However, it is possible that enzymatic systems exist in organisms which can break certain characteristic groups in molecules.

Although we do not rule out the possible role of metabolic transformation it seems unlikely that metabolic transformation is the sole cause of the low BCFs of some of the extensively halogenated aromatics.

BIOAVAILABILITY

Because of sorption to dissolved or particulate organic matter in the water phase, the total water concentration of many organic chemicals may not always reflect the fraction of chemical that is truly dissolved and thus believed to be available for uptake in fish. In such cases the concentration in the fish reflects only the available fraction of chemical in the water, which may be lower than the total concentration of chemical present in the water phase. Several authors have shown that the presence of humic acids and other organic matter in the water phase can reduce the

BCF significantly (McCarthy 1983, Landrum et al. 1985). This effect is likely to become more important when compounds become more hydrophobic, since a larger fraction of the chemical can be expected to exist in the sorbed state. Reduced bioavailability is therefore likely to contribute to the loss of linear correlation between the BCF and K_{ow} for the high K_{ow} compounds. However, the observation that chemicals such as hexabromobenzene (Zitko and Hutzinger 1976), some higher chlorinated naphthalenes (Opperhuizen et al. 1985) and PCDDs (Opperhuizen et al. 1985, Gobas et al. 1986a, Muir et al. 1986) have low BCFs compared to the more hydrophobic (higher K_{ow}) octa- and decachlorobiphenyl cannot be readily explained by reduced bioavailability.

Most sorption partition coefficients are satisfactorily correlated with K_{ow} but relatively few data exist for highly hydrophobic chemicals. It is possible that the conventional sorption correlations break down for such chemicals and that other factors such as molecular shape play an important role in determining sorption and bioavailability. At present knowledge about the extent to which hydrophobic chemicals are bioavailable to organisms in waters with a natural organic carbon level is scarce, but is of major importance for making reliable predictions about the bioaccumulation behaviour or toxicity of these chemicals.

MEMBRANE PERMEATION

It has been suggested that relatively large molecules, such as many of the high K_{ow} compounds, may experience a hindered membrane passage (Tulp and Hutzinger 1978, Muir et al. 1985, Kenaga and Goring 1980). In such cases uptake and elimination rate constants will be lower than expected. However, it is suspected that BCFs of conservative chemicals will not be affected by reduced membrane permeation provided exposure times are long

enough, since BCFs are inherently independent of kinetic factors.

It has also been shown (Mackay and Hughes 1984, Gobas et al. 1986a, Gobas and Mackay 1986) that most of the resistance for uptake and elimination of super hydrophobic chemicals lies in the aqueous phase of the fish and not in organic phases such as membranes. This implies that the membrane resistance has to increase by many orders of magnitude in order to affect uptake and elimination rates.

Based on the observed lack of bioconcentration of hexabromobenzene, hepta- and octachloronaphthalene and octachlorodioxin it has been suggested that molecules with certain spatial dimensions are not able to cross the membrane-water interface and enter the membrane (Opperhuizen et al. 1984 and 1985). These molecules, which were suggested to have minimal internal cross sections (MICS) of 0.96 nm or larger, are thus believed to have a low or zero bioconcentration factor. From a mechanistic point of view it seems conceivable that a cut-off diameter exists for passive membrane diffusion. However, what this cut-off diameter exactly is remains unclear since in a recent unpublished bioconcentration experiment brominated biphenyls with the same MICS as hexabromobenzene were accumulated in guppies (Gobas et al., 1987). The obvious test of this effect is to perform bioconcentration experiments with conservative chemicals varying in their spatial dimensions.

LIPID/WATER PARTITIONING

As pointed out earlier, the linear correlation between K_C and K_{ow} is the result of the similarity in phase properties of the fish lipids and 1-octanol towards organic chemicals i.e. y_L/y_o is constant. It can thus be argued that the loss of linear correlation between K_C and K_{ow} for high K_{ow} compounds may be due to the fact that y_L/y_o is no longer constant.

Two arguments support this contention:

a) the fish lipid phase consists primarily of biological membranes, in which the molecules are predominantly arranged in bilayers. The lipid phase thus has a distinct structure and restricted spatial dimensions. Since the 1-octanol phase is a bulk phase presumably with little or no structure, organic solutes may display different activity coefficients and partitioning behaviour in 1-octanol than in membranes.

b) it can be shown that the subcooled liquid solubility in 1-octanol i.e. $1/y_o$ decreases with an increase in the molar volume of the solute. This has been suggested previously (Miller et al. 1985) and is illustrated in Fig. 4.2, where x_o/F (i.e. $1/y_o$) of a series of high K_{ow} compounds is plotted versus the molar volume of the solute, calculated according to the Le Bas method (Reid et al. 1977). The values for x_o were obtained by measuring the solubilities of these chemicals in 1-octanol by a method described earlier (Miller et al. 1985) and from Anliker and Moser (1986). Since all chemicals were solids at the temperature of interest i.e. 25°C the fugacity ratio F was calculated as

$$F = \exp(\Delta S(1 - T_M/T)/R) \qquad (15)$$

where ΔS is the entropy of fusion at the melting point and estimated to be 13.5 calorie entropy units (Yalkowsky 1979), T_M (K) is the compound's melting point, T(K) is the experimental temperature and R is the gas constant i.e. 1.98 cal/mol.K. The experimentally obtained solubilities in 1-octanol and calculated fugacity ratios are listed in Table 4.3. It follows from Fig. 4.2 that all chemicals have mole fraction solubilities below 1 and accordingly activity coefficients above 1. This implies that these chemicals do not form ideal solutions in 1-octanol and that 1-octanol has a limited capacity to accommodate these chemicals. Figure

4.2 also shows that the log solubility in 1-octanol is approximately inversely related to the chemical's molar volume according to

$$\log y_o = 0.0051\ (+/-\ 0.0008) \cdot V - 0.26\ (+/-\ 0.32)$$
$$n = 41,\ r^2 = 0.80 \qquad (16)$$

showing that 1-octanol has a lower capacity to accommodate larger volume molecules.

As has been demonstrated convincingly by Kamlet et al., (1983) and Kamlet (1986), the best correlation of solubilities in solvents in general is achieved when both molar volume parameters and parameters expressing the interactions between solute and solvent are introduced. However, for solutes, which in this case are closely related chemically, variations in solubilities due to different solute-solvent interaction can be expected to be relatively small compared to the influence of the solute's varying molar volume. It may thus be concluded that the partitioning tendency of organic solutes in 1-octanol is not only determined by the behaviour of the solute in the water phase i.e. y_w but also by the behaviour in the organic phase. It also seems that for the class of aromatic compounds the formation of a cavity in 1-octanol of the dimensions of the solute molecule is the most important process determining the solute's subcooled liquid solubility. It can thus be expected that this cavity formation also governs the solubilities of these molecules in membranes. However, when solute molecules become relatively large i.e. have dimensions comparable to the thickness of the membrane phase, the structured membrane phase may not appear as a homogeneous phase to the solute, and specific interactions such as between the polar head groups of the phospholipids may have to be broken in order to dissolve the solute molecule in the hydrophobic interior of the membrane. It thus seems conceivable that for

relatively large solutes cavity formation in the membrane phase is relatively more difficult than for smaller molecules. Accordingly the subcooled liquid solubilities per unit of molar volume i.e. x/Fv of relatively large molecules can be expected to smaller and the activity coefficient per unit of molar volume i.e. y/v correspondingly higher than for smaller molecules. The expected behaviour of y_L and also of y_o with respect to molar volume for solutes, for which membrane/solute interactions are approximately equal is illustrated in Fig. 4.3. This figure shows that the relationship between K_{ow} and K_C cannot be linear but must be "parabolic" with a maximum value for K_C.

Preliminary work in our laboratory on membrane/water partitioning of hydrophobic compounds of varying molar volume supports this view. Partition coefficients between dymiristoyl-phosphatidylcholine (DMPC) membrane vessicles and water of chlorobenzenes, PCBs and PCDDs show a linear correlation with respect to the solute's molar volume up to a molar volume of 200 cm^3/mol. A maximum membrane-water partition coefficient of 10^6 was observed for solutes with a molar volume of approximately 300 cm^3/mol. For larger solutes the membrane-water partition coefficient tends to fall. If, as seems likely, artificial membranes do indeed simulate lipids in organisms better than 1-octanol then it is likely that the loss of linear correlation between K_C and K_{ow} is a least partly due to differences in solvent characteristics between natural lipids and 1-octanol. It is conceivable that there may emerge a "rule" that for molecules less than a certain volume or with certain dimensions, 1-octanol is satisfactorily surrogate, i.e. y_o and y_L are approximately equal. But for larger molecules this similarity breaks down and y_L is much larger than y_o and 1-octanol is no longer a satisfactory surrogate, and K_{ow} a

satisfactory descriptor. In that case membrane-water partition coefficients may be used as a more reliable but still simple method to estimate and correlate the bioconcentration factors of organic chemicals in aquatic organisms.

FISH GROWTH

If the fish is growing the term V_F in Eq. (1) is no longer constant and its time dependence must be included. The nature of the effect is that growth causes dilution, thus there is an apparent (but unreal) increase in k_2 or D_W. This effect can be included easily by adjusting Eq. (1). Elsewhere in these proceedings Thomann has discussed this issue in more detail.

CHEMICAL UPTAKE FROM FOOD

Chemical uptake from food and chemical excretion to the faeces can also be included in the differential equation describing chemical uptake in fish. We do not report here a full account of this issue but we report on some recent findings.

For substances of relatively low K_{ow} (i.e., $\log K_{ow} < 5$), the chemical exchange between fish and water (via the gills) is relatively fast compared to the chemical uptake from food and excretion to the faeces. As a result the chemical ingested with the food is rapidly equilibrated with the water through gill exchange and the concentration in the fish will approach or achieve equilibrium with the water. Therefore it does not matter if the fish obtains the chemical from the water or food. In that case the bioaccumulation factor due to combined chemical uptake from water and food corresponds to the bioconcentration factor measured in laboratory experiments and, when not metabolized, can be correlated with the 1-octanol-water partition coefficient. For these chemicals there is

little or no biomagnification.

As K_{ow} increases, the time needed to release the chemical to the water increases. The fish may thus achieve a state in which the rate of intake from food exceeds the release rate, which can result in a fish concentration or fugacity exceeding the equilibrium value. This phenomenon, which is discussed in more detail elsewhere (Gobas et al. 1987), is generally referred to as biomagnification. We believe that the mechanism underlying this process is that as a result of food digestion in the gastro-intestinal tract the organic mass in the GI-tract continuously decreases thus increasing the chemical's concentration or fugacity in the GI-tract and driving the chemical across the gut wall into the fish.

A fish may then live in water contaminated with a chemical, which has a fugacity in the water of for example 10^{-6} Pa and eat small organisms with a similar chemical fugacity, but achieve a chemical fugacity of perhaps $4 \cdot 10^{-6}$ Pa. This increase in the chemical's fugacity takes place at every trophic level of the food chain, i.e., where one organism feeds on another organism of a lower trophic level. So, if the fish with a chemical fugacity of $4 \cdot 10^{-6}$ is eaten by another organism of a higher trophic level, that organism may reach a chemical fugacity of $16 \cdot 10^{-6}$ Pa. It appears from our work that fish eating birds such as herring gulls achieve a chemical fugacity increase of approximately 10 to 30. This biomagnification phenomenon appears to be of the order of a factor of 3 to 5 per trophic level for aquatic organisms and predominantly applies to chemicals with a log K_{ow} between 5 and 7. At higher K_{ow} values we suspect that the efficiency of gut absorption efficiency decreases (Gobas et al. 1987). These chemicals may therefore not biomagnify or even bioconcentrate appreciably.

It is worth noting that from a regulatory standpoint that this phenomenon is desirable, but it is essential to understand its cause since it is conceivable that chemicals may exist of high K_{ow} which do bioaccumulate. In addition it should be noted that bioconcentration data for chemicals with log K_{ow} exceeding 7 is extremely scarce. Conclusions about their bioaccumulation potential are therefore difficult to draw.

We are presently working to assemble and validate models describing these processes. We focus our attention on chemicals of very high K_{ow} (i.e., log K_{ow} between 5 and 8) since they are the chemicals with the highest expected bioaccumulation potential.

CONCLUSIONS

In this paper we have discussed the factors that may affect the linear correlation between bioconcentration factors in fish and the 1-octanol-water partition coefficient. Since a lipid-water partitioning process is the principal process controlling the uptake of organic chemicals from the water the same factors may also affect other QSARs in aquatic toxicology.

For compounds with log K_{ow} between 1 and 5 correlations between K_{ow} and K_C are generally linear. When deviations from linear behaviour occur, metabolic transformation has to be considered the principal reason for this effect, since all other factors influencing K_{ow} - K_C relationships apply only to high K_{ow} compounds.

For compounds with log K_{ow} exceeding 5 or 6 simple linear relationships between K_C and K_{ow} breakdown. In laboratory experiments involving chemical exchange between water and fish K_C often shows a maximum for compounds with log K_{ow} of 5 to 6 and then tends to fall for compounds with log K_{ow} exceeding 6. For these chemicals an equilibrium

between fish and water is reached only after a very long exposure time, which often exceeds the experimental exposure time, such that it is often difficult to determine the actual steady state level in the fish and thus the true bioconcentration factor. Indeed the required exposure time may exceed the lifetime of the fish. However, even when curve fitting or extrapolation procedures are used to determine steady state concentrations in the fish, the calculated bioconcentration factors are still lower than would be expected from their high K_{ow}. The combination of a relatively short exposure time, slow uptake and the "diluting" effect of fish growth does therefore not explain the relatively low bioconcentration factors of the high K_{ow} compounds.

The decrease in subcooled liquid solubility of organic solutes in 1-octanol with increasing molar volume shows that the partitioning tendency of these chemicals is not only determined by their behaviour in the water phase i.e. their hydrophobicity or y_W but also by their behaviour in the organic medium. It is conceivable that differences in phase characteristics between 1-octanol and the organism lipids towards organic solutes affect the relationship between 1-octanol-water and fish lipid/water partition coefficients. Preliminary studies on membrane/water partition coefficients indicate that lipid phases in organisms, which predominantly consist of membranes, may have a relatively low potential to accommodate larger molar volume molecules, many of which have high K_{ow}. It seems therefore conceivable that the relatively low solubility of voluminous molecules in membranes compared to 1-octanol is one of the causes of the loss of linear correlation between K_C and K_{ow}.

A second reason for the loss of this linear correlation can be a reduced bioavailability of high K_{ow} compounds. Unfortunately experimental

data which can distinguish between the bioavailable and non-bioavailable fraction of (super) hydrophobic chemicals in water are scarce because of the extreme experimental difficulty of making these measurements. As a result, no accurate predictions can yet be made about the role of a reduced bioavailability on the linearity of correlations between K_C and K_{ow}.

Under field conditions, where a fish is exchanging chemical between water and food, correlation between the bioaccumulation factor and the 1-octanol-water partition coefficient also show a loss of linear correlation. For high K_{ow} chemicals bioaccumulation factors are often higher than would be predicted from the 1-octanol-water partition coefficient. This is probably the result of biomagnification which can result in fish-water concentration ratios which exceed the fish-water partition coefficients determined in the laboratory.

We conclude that when assessing the behaviour of new and existing chemicals it is unwise to extrapolate existing $K_{ow} - K_C$ correlations into the super-hydrophobic region. It is believed that a chemical by chemical assessment will be needed in which the roles of metabolism, bioavailability, membrane permeation, lipid/water partitioning, fish growth and food uptake are considered as modifying the basic equilibrium relationship. Some of these phenomena are fortunate in that they mitigate the bioaccumulation tendencies of many chemicals but, since these chemicals have a very high bioaccumulation potential and are potentially very toxic, it seems unwise to exploit or depend on these factors without fully understanding their nature. The phenomenon of food chain accumulation has to be examined carefully since it is likely to result in very high concentrations in organisms of higher trophic level.

Finally, we believe that progress towards assembling a comprehensive model of chemical uptake in fish, including equilibria, kinetics and food chain effects (i.e., biomagnification) is best achieved by assembling models of various types, testing them and modifying them to improve the fidelity with which they describe bioaccumulation.

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REFERENCES

Abernethy, S., and Mackay, D., (1987). "A Discussion of Correlations for Narcosis in Aquatic Species", in "QSAR in Environmental Toxicology II", K.L.E. Kaiser (ed.), D. Reidel Publishing Company, Dordrecht, the Netherlands.

Anliker, R., and Moser, P., (1986). "The Limits of Bioaccumulation of Organic Pigments in Fish: Their Relation to Their Partition Coefficient and the Solubility in Water and Octanol", Poster presented at the 2nd International Workshop on QSAR in Environmental Toxicology, Hamilton, Ontario, June 9–13.

Bobra, A., Shiu, W.Y., and Mackay, D., (1985). "Quantitative Structure Activity Relationships for the Acute Toxicity of Chlorobenzenes to Daphnia Magna", Environmental Toxicology Chem. 4, 297–305.

Branson, D.R., Takahashi, I.T., Parker, W.M., and Blau, G.E., (1986). "Bioconcentration Kinetics of 2, 3,7, 8-tetrachlorodibenzo-p-dioxin in Rainbow Trout", Environmental Toxicology Chem. 4, 779–788.

Bruggeman, W.A., Opperhuizen, A., Wijbenga, A , and Hutzinger, O., (1984). "Bioaccumulation of Super-lipophilic Chemicals in Fish", Environmental Toxicology Chem 7, 173-189.

Dearden, J.C., (1985). "Partitioning and Lipophilicity in Quantitative Structure Activity Relationships", Environmental Health Persp. 61, 203-228.

Gobas, F.A.P.C., Opperhuizen, A., and Hutzinger, O.,(1986a). "Bioconcentration of Hydrophobic Chemicals in Fish: Relationship with Membrane Permeation", Environmental Toxicology Chem. 5, 637-646.

Gobas, F.A.P.C., and Mackay, D., (1986). "Dynamics of Hydrophobic Organic Chemical Bioconcentration in Fish", Environmental Toxicology Chem. 6, 495-504.

Gobas, F.A.P.C., Shiu, W.Y., Mackay, D., and Opperhuizen, A., (1986b). "Bioaccumulation of PCDDs and OCDF in Fish After Aqueous and Dietary Exposure", Chemosphere 15, 1985-1986.

Gobas, F.A.P.C., Shiu, W.Y., and Mackay, D., (1987). "Factors Determining Partitioning of Hydrophobic Organic Chemicals in Aquatic Organisms", In K.L.E. Kaiser ed., QSAR in Environmental Toxicology. D. Reidel Publishing Company, Dordrecht, 107-123.

Gobas, F.A.P.C., Muir, D.C.G., and Mackay, D., (1987). "Dynamics of Dietary Bioaccumulation of Hydrophobic Organic Chemicals in Fish", Chemosphere submitted.

Hawker, D.W., and Connell, D.W., (1985). "Relationship Between Partition Coefficient, Uptake Rate Constant, Clearance Rate Constant and Time to Equilibrium for Bioaccumulation", Chemosphere, 14, 1205-1219.

Hermens, J., Konemann, H., Leeuwangh, P., and Musch, A., (1985). "Quantitative Structure Activity Relationships in Aquatic Toxicity Studies of Chemicals and Complex Mixtures of Chemicals", Environmental Toxicology Chem. 4, 273-279.

Kamlet, M.J., Abboud, J.L.M., Abraham, M.H., and Taft, R.W., (1983). "Linear Solvation Energy Relationships. 23. A Comprehensive Collection of the Solvatochromic Parameters and Some Methods for Simplifying the Generalized Solvatochromic Equation", J. Org. Chem., 48, 2877-2887.

Kamlet, M.J., (1986). Paper presented at the 2nd International Workshop on QSAR in Environmental Toxicology, Hamilton, Ontario, June, 9-13.

Kenaga, E.E., and Goring, C.A.I., (1980). "Relationship Between Water Solubility and Soil Sorption, Octanol-water Partitioning and Bioconcentration of Chemicals in Biota", in "Aquatic Toxicology", Eaton, J.G., Parrish, P.R.P., and Hendricks, A.C., (eds.) STP 707, American Society for Testing of Materials, Philadelphia, 78-115.

Landrum, P.F., Reinhold, M.D., Nihart, S.R., and Eadie, B.J., (1985). "Predicting the Bioavailability of Organic Xenobiotics to Pontoporeia Hoyi in the Presence of Humic and Fulvic Materials and Natural Dissolved Organic Matter", Environmental Toxicology Chem. 4, 459–467.

Mackay, D., (1982). "Correlation of Bioconcentration Factors", Environmental Sci. Technol. 16, 274–278.

Mackay, D., and Patterson, S., (1982). "Fugacity Revisited", Environ. Sci. Technol. 16, 654A–660A.

Mackay, D., and Hughes, A.I., (1984). "Three–parameter Equation Describing the Uptake of Organic Compounds by Fish", Environ. Sci. Technol. 8, 439–444.

McCarthy, J.F., (1983). "Role of Particulate Organic Matter in Decreasing Accumulation of Poly Nuclear Aromatic Hydrocarbons by Daphnia Magna", Arch. Environ. Contam. Toxicol. 12, 559–568.

Miller, M.M., Wasik, S.P., Huang, G.L., Shiu, W.Y., and Mackay, D., (1985). "Relationship Between Octanol–water Partition Coefficient and Aqueous Solubility", Environ. Sci. Technol. 19, 522–529.

Muir, D.C.G., Yarechewski, A.L., Knowll, A., Webster, G.R.B., (1986). "Bioconcentration and Disposition of 1, 3, 6, 8–tetrachlorodibenzo–p–dioxin and octachlorodibenzo–p–dioxin by Rainbow Trout and Fathead Minnows", Environ. Toxicol. Chemi. 5, 261–272.

Muir, D.C.G., Marshall, W.K., and Webster, W.R.B., (1985). "Bioconcentration of PCDDs by Fish: Effects of Molecular Structure and Water Chemistry", Chemosphere 14, 829–833.

Mullins, L.J., (1954). "Some Physical Mechanisms Innarcosis", Che. Rev. 54, 289–323.

Neely, W.B., Branson, D.R., and Blau, G.E., (1974). "Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish", Env. Sci. Technol. 8, 1113–1115.

Oliver, B.G., and Niimi, A.J., (1985). "Bioconcentration Factors of Some Halogenated Organics for Rainbow Trout: Limitations in Their Use for Predicting of Environmental Residues", Environ. Sci. Technol. 19, 842–848.

Opperhuizen, A., Van de Velde, E.W., Gobas, F.A.P.C., Liem, D.A.K., Van der Steen, J.M.D., and Hutzinger, O., (1985). "Relationship Between Bioconcentration in Fish and Steric Factors of Hydrophobic Chemicals", Chemosphere 14, 1871–1896.

Opperhuizen, A., Gobas, F.A.P.C., and Hutzinger, O., (1984). "Unmetobolized Compounds: Their Properties and Implications", in J. Caldwell and G.D. Paulson, eds, in "Foreign Compound Metabolism", Taylor and Francis, London, 109–117.

Opperhuizen, A., Wagenaar, W.J., Van der Wielen, F.W.M., Van den Berg, M., Olie, K., and Gobas, F.A.P.C., (1986). "Uptake and Eliminiation of PCDD/PCDF Congeners by Fish after Aqueous and Dietary Exposure to a Fly-ash Extract from a Municipal Incinerator", Chemosphere 15, in press.

Reid, R.C., Prausnitz, J.M., and Sherwood, T.K., (1977). "The Properties of Gases and Liquids", 3rd ed., McGraw-Hill, New York.

Shiu, W.Y., Mackay, D., (1986). "A Critical Review of Aqueous Solubilities, Vapor Pressures, Henry's law Xonstants, and Octanol-water Partition Coefficients of the Polychlorinated Biphenyls", J. Phys. Chem. Ref. Data, 15, 911-929.

Southworth, G.R., Keffer, C.C., and Beauchamp, J.J., (1980). "Potential and Realized Bioconcentration. A Comparison of Observed and Predicted Bioconcentration of Azaarenes in the Fathead Minnow (pimephales promelas)", Environ. Sci. Technol., 1529-1531.

Safe, S., (1984). "Polychlorinated Biphenyls (PCBs) and Polybrominated (PBBs): Biochemistry, Toxicology and Mechanism of Action", CRC Critical Reviews in Toxicology 13, 319-395.

Spacies, A., Landrum, P.F., and Leversee, G.J., (1983). "Uptake Depuration, and Biotransformation of Anthracene and benzo-a-pyrene in Bluegill Sunfish", Ecotox. Environ. Safety 7, 330-341.

Tulp, M.Th.M., and Hutzinger, O., (1978). "Some Thoughts on the Aqueous Solubilities and Partition Coefficients of PCB and the Mathematical Correlation Between Bioconcentration and Physico Chemical Properties", Chemosphere 7, 849-860.

Veith, G.D., Call, D.J., and Brooke, L.T., (1983). "Structure Toxicity Relationships for the Fathead Minnow, Pimephales; Narcotic Industrial Chemicals", Can. J. Aquat. Sci. 40, 743-748.

Yalkowsky, S.H., (1979). "Estimation of Entropies of Fusion of Organic Compounds", Ind. Eng. Chem. Fundam. 18, 108-111.

Zitko, V., and Hutzinger, O., (1976). "Uptake of Chloro- and Bromobiphenyls, Hexachlorobromobenzene by Fish", Bull. Environ. Contam. Toxicol. 16, 665-673.

TABLE 4.1: Chemical Abstract Numbers (CAS), Octanol/Water Partition Coefficients (log kow) BCFs in Whole Fish (log kc) and in lipids (log K1) in the guppy (Poecilia reticulata)

COMPOUND	CAS Number	Log Kow	Log Kc	Log K1
2,5 DICHLOROBIPHENYL	34883-39-1	5.10 a	4.26	5.72 d
2,2,5,5 TETRACHLOROBIPHENYL	35693-99-3	6.10 a	4.92	6.38 d
2,2,4,4,5,5 HEXACHLOROBIPHENYL	35065-27-1	6.90 a	5.32	6.78 d
2,2,3,3,4,4,5,5, OCTACHLOROBIPHENYL	35694-08-7	7.10 a	4.35	5.81 d
DECACHLOROBIPHNEYL	2051-24-3	8.26 a	4.02	5.48 d
HEXABROMOBENZENE	87-82-1	> 6.0		< 5.0 b,d
2-MONOCHLORONAPHTHALENE	91-58-7	3.90 b	3.63	4.81 b
1,4 DICHLORONAPHTHALENE	1825-31-6	4.66 b	3.36	4.54 b
1,8 DICHLORONAPHTHALENE	2050-74-0	4.19 b	3.79	4.96 b
2,3 DICHLORONAPHTHALENE	2050-75-1	4.51 b	4.04	5.22 b
2,7 DICHLORONAPHTHALENE	2198-77-8	4.56 b	4.04	5.22 b
1,3,7 TRICHLORONAPHTHALENE	1321-65-9	5.35 b	4.43	5.61 b
1,2,3,4 TETRACHLORONAPHTHALENE	20020-02-4	5.75 b	4.66	5.71 b
1,3,5,7 TETRACHLORONAPHTHALENE	53555-64-9	6.19 b	5.06	5.71 b
1,3,5,8 TETRACHLORONAPHTHALENE	31604-28-1	5.81 b	4.69	5.57 b
PENTACHLOROBENZENE	608-93-5	5.03 c	4.38	5.40 b
2,3',4',5 TETRACHLOROBIPHENYL	70632-48-0	5.90 a	4.92	5.50 b
1,4 DICHLOROBENZENE	106-46-7	3.38 c	1.99	3.25 e
1,2,3 TRICHLOROBENZENE	87-61-6	4.04 c	2.84	4.11 e
1,3,5 TRICHLOROBENZENE	108-70-3	4.02 c	2.88	4.14 e
1,2,3,5 TETRACHLOROBENZENE	634-90-2	4.65 c	3.59	4.83 e
PENTACHLOROBENZENE	608-93-5	5.03 c	4.14	5.41 e
HEXACHLOROBENZENE	118-74-1	5.45 c	4.19	5.46 e
2,7, DICHLORODIBENZO-P-DIOXIN	33857-26-0	5.75 g	1.7	2.9 f
1,2,4 TRICHLORODIBENZO-P-DIOXIN	39227-58-2	6.45 g	1.9	3.1 f
1,2,3,4 TETRACHLORODIBENZO-P-DIOXIN	30746-58-8	6.70 g	2.2	3.4 f
OCTACHLORODIBENZO-P-DIOXIN	3268-87-9	8.40 g	1.9	3.1 f

a: from Shiu and Mckay
b: from Opperhuizen et al. 1985
c: from Miller et al. 1985
d: from Bruggeman et al. 1984
e: from Konemann et al. 1980
f: from Gobas et al. 1986b
g: from Andren et al. 1987

Table 4.2: Experimentally observed (exp) and correlated (cor) bioconcentration factors (Kc) and metabolic rate constants (k_R) (1/hr) in fish.

COMPOUND	log Kow	$K_{c,exp}$	$K_{c,cor}$	k_1	$k_{R,exp}$	$k_{R,cor}$
ANTHRACENE (1)	4.45	675	1350	36	0.027	0.027
BENZO-a-PYRENE (1)	6.06	490	55100	49	0.31	0.1
ACRIDINE (2)	3.3	100	96		0	0
BENZ[a]ACRIDINE (2)	4.45	106	1350	100	0.49	0.87
DIBENZ[a,h]ACRIDINE (2)	5.6	107	19100	12	0.18	0.11

(1) Spacie et al., 1983
(2) Southworth et al., 1980

TABLE 4.3: CAS numbers, molecular weight, melting point (Tm), molecular weight (Mw), fugacity ratio (F), solubility in 1-octano (Cs), activity coefficient (log yo), and 1-octanol/water partition coefficient (log kow)

COMPOUND	CAS Number	MOL.W.	TM (K)	V(cm3/mol)	F	C(s)mol/l	Log yo	Log Kow
4 monochlorobiphenyl	2051-62-9	188.7	351	206	2.08E-01	6.08E-01	0.56	4.50
4,4 dichlorobiphenyl	2050-68-2	223.1	422	226	5.46E-02	7.13E-02	0.78	5.30
2,4,5 trichlorobiphenyl	15862-07-4	257.5	350	247	2.92E-01	1.76E-01	1.12	5.60
2,2,5,5 tetrachlorobiphenyl	35693-99-3	292	360	268	2.28E-01	2.34E-01	0.89	6.10
2,3,4,5 tetrachlorobiphenyl	33284-53-6	292	364	268	2.09E-01	1.40E-01	1.07	5.90
decachlorobiphenyl	2051-24-3	487.7	579	394	1.48E-03	1.69E-03	0.84	8.26
naphthalene	91-20-3	128.2	353	148	2.68E-01	9.59E-01	0.34	3.35
biphenyl	92-52-4	154.21	343	185	3.42E-01	6.91E-01	0.59	3.95
acenaphthene	83-32-9	154.21	369	173	1.85E-01	2.56E-01	0.76	3.92
fluorene	86-73-7	154.21	389	188	1.17E-01	2.24E-01	0.62	4.18
1-methyl-fluorene	1730-37-6	168.21	358	210	2.39E-01	2.98E-01	0.80	4.97
anthracene	120-12-7	178.2	489	197	1.17E-02	1.18E-02	0.89	4.54
phenathrene	85-01-8	178.2	374	199	1.66E-01	4.01E-01	0.51	4.57
fluoranthene	206-44-0	202.3	384	217	1.32E-01	1.73E-01	0.78	5.22
pyrene	129-00-0	202.3	429	214	4.67E-02	1.40E-01	0.42	5.18
chrysene	218-01-9	228.3	528	251	4.78E-03	2.00E-03	1.28	5.79
2,3 benzofluorene	243-17-4	216.28	482	240	1.38E-02	1.77E-02	0.79	5.75
perylene	198-55-0	252.3	550	263	2.88E-03	3.04E-03	0.87	6.50
1,2,5,6 dibenzanthracene	53-70-3	278.35	539	300	3.71E-03	9.38E-04	1.49	7.19
From Mosar and Anliker:								
DDT	50-29-3	354.48	382	364	1.37E-01	8.18E-02	1.12	6.36
hexachlorocyclohexane	319-84-6	290.82	433	259	4.24E-02	5.16E-02	0.81	3.80
hexachlorobenzene	118-74-1	284.76	503	221	8.46E-03	1.53E-02	0.64	5.47
1,4 dichlorobenzene	106-46-7	147	326	138	4.99E-01	1.77E+00	0.35	3.38
1,2,4 trichlorobenzene	120-82-1	181.45	290	159	1.00E+00		0.00	3.98
CIBA-GEIGY LIPOPHILIC DYE #:								
I		546.38	448	565	3.00E-02	1.48E-04	3.20	2.50
II		333	498	349	9.49E-03	3.00E-04	2.40	3.40
III		363	498	422	9.49E-03	3.31E-04	2.36	>4.0
IV		368.19	492.2	364.6	1.09E-02	4.62E-04	2.27	>4.0
V		448.53	421.2	552.3	5.59E-02	9.14E-04	2.68	4
VI		423.3	457.2	541.6	2.44E-02	1.89E.03	2.01	>2.0
VII		426.9	443.2	459.5	3.37E-02	2.23E-03	2.08	4
VIII		528	390.2	528.3	1.14E-01	3.16E-03	2.46	4.1
IX		373.83	419.2	428.7	5.86E-02	5.62E-03	1.92	3.9
X		411.54	446.2	504	3.14E-02	5.90E-03	1.62	4.5
XI		340.33	549.2	399.2	2.93E-03	2.76E-05	2.92	3.82
XII		307.29	563.2	368.7	2.12E-03	5.53E-05	2.48	5.4
XIII		486.76	563.2	546.2	2.12E-03	1.60E-05	3.02	8.38
XIV		629.5	593.2	735	1.06E-03	7.94E-07	4.02	6.8
XV		726.44	593.2	823.2	1.06E-03	6.33E-07	4.12	8.1
XVIII		439.78	603.2		8.45E-04	7.96E-06	2.92	3.4
XIX		312.32	673.2	342.2	1.68E.04	5.44E-06	2.39	4.3
XX		1100	753.2	960	2.673-05	6.36E-08	3.52	17.4

STRUCTURAL FORMULAS FOR THE LISTED LIPOPHILIC DYES CAN BE FOUND IN ANLIKER AND MOSAR (1986).

11267-108.1

FIGURE CAPTIONS

Fig. 4.1. Bioconcentration factors based on fish lipid weights of chlorobenzenes (ClB), PCBs, polychlorinated naphtalenes (PCN), chlorinated dibenzo-p-dioxins (PCDD) in Poecilia reticulata (guppy) as a function of K_{ow}.

Fig. 4.2. Activity coefficients of chlorinated aromatics, polynuclear aromatics and lipophilic dyes in 1-octanol as a function of molar volume.

Fig. 4.3. The expected behaviour of the activity coefficient of chemically related compounds in water (W), 1-octanol (O) and lipid tissues of organisms (1) versus molar volume, v.

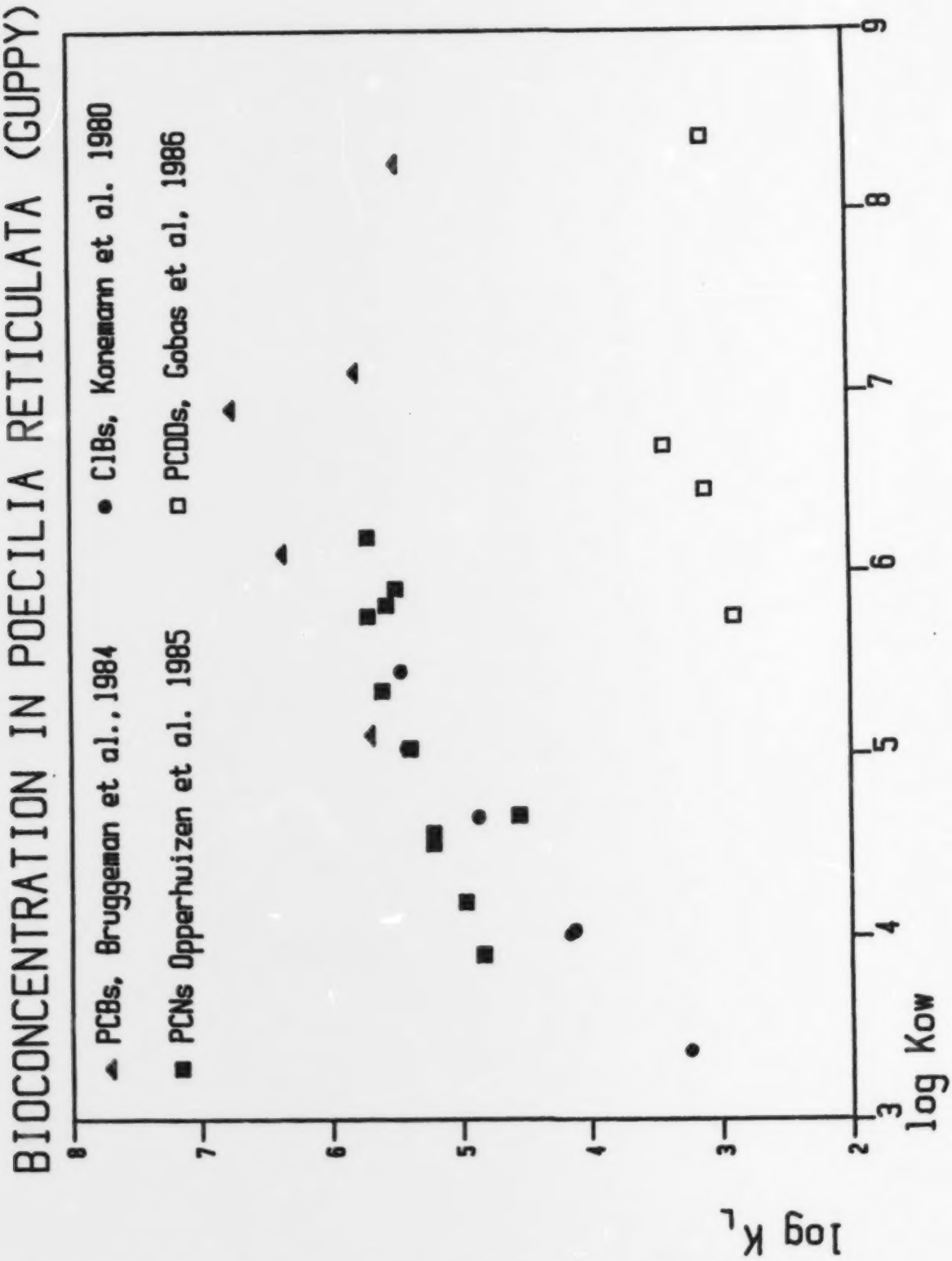

Figure 4.1: Bioconcentration factors based on fish lipid weights of chlorobenzenes (ClB), PCBs, polychlorinated naphthalenes (PCN), chlorinated dibenzo-p-dioxins (PCDD) in Poecilia reticulata (guppy) as a function of Kow.

Figure 4.2: Activity coefficients of chlorinated aromatics, polynuclear aromatics and lipophilic dyes in 1-octanol as a function of molar volume.

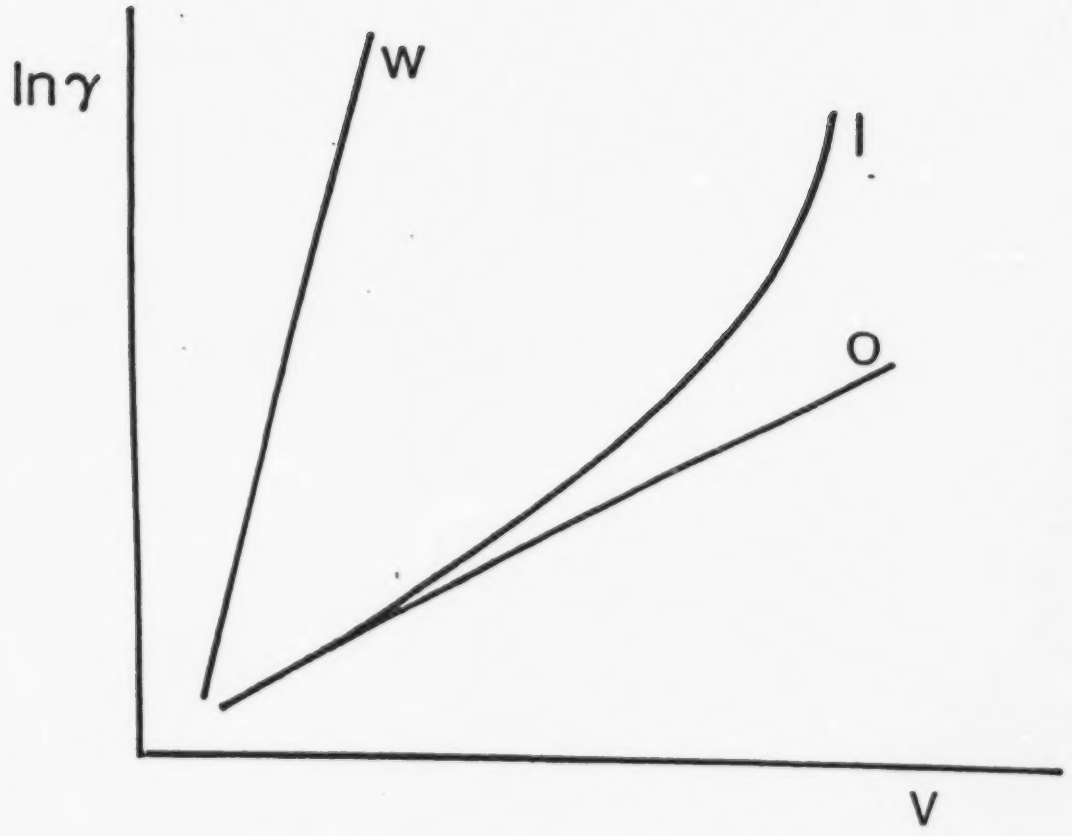

Figure 4.3: The expected behaviour of the activity coefficient of chemically related compounds in water (W), 1-octanol (O) and lipid tissues of organisms (l) versus molar volume, v.

CHAPTER 5

BIOACCUMULATION OF ORGANIC CHEMICALS IN GREAT LAKES BENTHIC FOOD CHAINS

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INTRODUCTION

The benthic food chain is an important component of the transport and ecosystem fate of organic chemicals in the Great Lakes. Benthic animals can significantly alter the physical and chemical properties of sediments, thus affecting constituent mass fluxes across the sediment-water interface. Sediment exposures can cause accumulation of organic chemicals in benthic animals, with the potential for subsequent trophic transfer to higher predators.

The impetus for this work was the desire of the Ontario Ministry of the Environment to incorporate an aquatic food chain component into existing transport and fate models for organic chemicals in the Great Lakes. The goal of this overall effort is to identify essential state variables and process mechanisms that govern the fate of these chemicals in aquatic ecosystems. Most of the existing research in this area has been on the pelagic food chain. Comparatively little is known about organic chemical dynamics in the benthic food chain.

Scope

The focus in this paper is on the benthic component of the overall aquatic food chain. Emphasis is placed on the effects of sediment exposures on benthic animals, and on the potential for trophic transfer to higher predators. Results from this work have direct implications for the degree of model complexity required to describe organic chemical dynamics and fate in the benthic food chain. For completeness, a brief review of pertinent literature is presented on the effects of benthic animals on the physical-chemical properties of sediments. Results from this review may have implications for th physical-chemical component of the overall ecosystem model.

STRUCTURE OF BENTHIC FOOD CHAIN

There is considerable uncertainty regarding the structure and function of the benthic food chains in the Great Lakes. Flint (1986) has recently developed a comprehensive conceptual model of the Lake Ontario deepwater food web. The model is based on a synthesis of existing information on standing stocks, production rates and potential trophic linkages. Figure 5.1 contains a schematic diagram of the hypothesized trophic relationships and Fig. 5.2 contains a schematic analysis of annual carbon production and energy flow in this food web. Oliver and Niimi (1987) have proposed a more simplified model of the Lake Ontario food chain (Fig. 5.3).

The principal differences between these two models are in the coupling between the benthic and pelagic food chains. The Flint model contains direct linkages between macrobenthos (oligochaetes, chironomids and amphipods) and adult alewives, smelt, and large fish (primarly salmonids) in the pelagic food chain. The Oliver and Niimi model does not contain these linkages. Furthermore, the Flint model links sculpins (benthic fish) to smelt (pelagic food chain), whereas the Oliver and Niimi model links sculpins directly to large fish. Despite uncertainties in actual trophic linkages, it is clear that the main food source for the benthic community is from phytoplankton photosynthesis and phytoplankton-derived detritus from the overlying waters.

The structure of the benthic food chain has implications for the types of models required to describe the distribution of contaminants. Thomann and Connolly (1984) and Oliver and Niimi (1987) have shown that chemical concentrations in the pelagic food chain depend on the trophic position of the animal, especially the number of trophic transfers in the food uptake

pathway. In the benthic food chain simple empirical models may suffice for animals at low trophic levels, while mechanistic food chain models may be required for animals at higher trophic levels.

EFFECTS OF BENTHOS ON PHYSICAL-CHEMICAL PROPERTIES OF SEDIMENTS

Benthic organisms can have significant effects on the physical and chemical properties of sediments and hence, on the entire sediment exposure environment. Lee and Swartz (1980) have reviewed the mechanisms and rates of biodeposition and bioturbation in the marine environment. They concluded that the major biogenic processes modifying sediments are biodeposition, particle transport, fluid transport, stabilizing mechanisms and macrofaunal-microbial interactions. In their opinion, there is currently a basic understanding of biodeposition and particle transport, but not of the latter three processes.

McCall and Tevesz (1982) have reviewed the effects of freshwater benthos on physical properties of bottom sediments. They focused on macrobenthos (adult length > 1 mm) because, in their opinion, too little is known about freshwater meio- and microbenthos. McCall and Fisher (1980) studied the effects of tubificid oligochaetes on Lake Erie sediments and concluded that the oligochaetes could alter grain size, settling velocity, erodibility, porosity, permeability, vertical gradients of particulate and dissolved sedimentary materials, diffusive fluxes and sediment oxygen demand. Observed variations in these parameters ranged from factors of 2 to 10 in the presence of the tubificid oligochaetes. McCall et al. (1979) studied sediment reworking activities of unionid bivalves in Lake Erie and found that they plow the top 10 cm and they pump large quantities of water through the sediment. These filter-feeding clams are the largest invertebrates in Lake Erie and they account for

most of the secondary production in the western basin.

Robbins (1986) developed a model to describe the processes of sediment diagenesis and the effects of biogenic reworking by conveyer-belt, deposit-feeding benthic organisms (e.g., tubificid oligochaetes). The model is based on transport and chemical reaction and it includes compaction, diffusion and advective redistribution by the benthic organisms. Robbins concluded that particle diffusion, as well as advection, was required to accurately describe the distributions of highly sorbed tracer constituents.

Karickhoff and Morris (1985) used laboratory microcosms to study the transport of hydrophobic pollutants in bottom sediments in the presence of oligochaete worms, as contrasted to transport by molecular diffusion. They found that in the presence of stable worm populations, pollutant transport within the biologically mixed surface layer was entirely worm mediated. More than 90 percent of the chemicals in this layer were transported to the sediment surface in a 30–50 day period. Sediment was vertically pumped to the surface at rates from 9 to 30 times faster than by maximum molecular diffusion rates for the highly sorbed chemicals used in the experiments. Mass flux from sediment to water column, however, was only enhanced by a factor of 4 to 6. The mitigating process was sediment pelletization which trapped sorbed chemicals and significantly retarded chemical release into the aqueous phase at the sediment-water interface.

Gschwend et al. (1986) have proposed a modeling framework to predict the transfer of hydrophobic organic chemicals between bed sediments and overlying waters. The principal components in this framework are a description of the microscopic scale process of sorption kinetics and models of the exposure of bed particles to adjacent waters of varying

composition. Effects due to diffusion of solutes in interstitial fluids, biological mixing of surficial sediments and suspension of bed solids are included.

BIOACCUMULATION BY AQUATIC ORGANISMS

Environmental contaminants can be accumulated by fish and benthic organisms through direct uptake from water and through food chain uptake. The primary mode of accumulation in a particular case depends on the properties of the chemical, the relative concentrations of the chemical in the water and food, and on the trophic position of the animal.

The term bioconcentration refers to accumulation of a chemical in fish by transport through the gill or other membranes, and it excludes accumulation by the consumption and absorption of contaminated food (Veith et al. 1979). Bioconcentration is usually expressed in terms of a bioconcentration factor (BCF) which is the ratio of the chemical concentration in the fish to the chemical concentration in the water under equilibrium conditions. The term biomagnification refers to accumulation of chemicals through contaminated food.

Bioconcentration is generally viewed as a simple phase partitioning process. Neely et al. (1974) observed that the bioconcentration of organic chemicals in trout followed a linear relationship with the octanol-water partition coefficient (K_{ow}) of the chemicals. Veith et al. (1979) extended this concept to a larger range of organic chemicals using uptake experiments with fathead minnows. They pointed out that laboratory-derived BCFs were only a conservative estimate of actual environmental residues because these residues are the result of potential biomagnification, as well as bioconcentration.

Mackay (1982) examined the physical-chemical factors influencing bioconcentration of organic chemicals and concluded that there was a sound theoretical basis for expecting a good correlation between BCF and K_{ow}. His arguments were based on the assumption that an organism, such as a fish, could be viewed as consisting of one or more phases of differing chemical composition and volume fraction. At equilibrium the chemical potential, or fugacity, of the bioconcentrating chemical will be equal in the exposure medium and in each phase.

Chiou (1985) also demonstrated that K_{ow} was a good predictor for lipid-water partition coefficients and for BCFs in fish. He pointed out that discrepancies can occur between BCF and K_{ow} under the following conditions: first, chemicals that are unstable in water or that are readily metabolized by animals will not reach an equilibrium state; second, BCF values obtained with exposure times that are too short may not represent true equilibrium between the biotic and water phases; and third, macromolecular organic molecules (e.g., humic substances) could enhance the apparent solubility of relatively insoluble chemicals, thus decreasing the computed BCF value.

Several studies have demonstrated the importance of exposure levels and times to equilibrium in developing valid correlations between BCF and K_{ow}. Oliver and Niimi (1983) studied bioaccumulation of ten chlorobenzenes by rainbow trout over a 119-day exposure period in the laboratory. They observed that time to equilibrium was dependent on the exposure level and the degree of chlorine substitution. Good correlations were obtained between BCF and K_{ow} for chemicals that reached equilibrium ($\log K_{ow} < 5$); however, hexachlorobenzene only obtained equilibrium at a high exposure level, not at a lower exposure. Good agreement was obtained

using their laboratory-based BCFs to predict fish concentrations in Lake Ontario from ambient concentration levels, except for hexachlorobenzene. In a subsequent study, Oliver (1984) found that concentration factors for 24 organic chemicals in oligochaete worms continued to increase over a 110-day exposure to naturally contaminated Lake Ontario sediments. Inconsistent relationships were observed between the BCF and K_{ow} values for the different chemicals.

There are considerable reported differences in the relative importance of water vs food uptake even for organisms at the base of the benthic food chain. For example, Adams et al. (1985) studied kepone uptake by chironomids and concluded that bioaccumulation occurs primarily via interstitial water and not from ingestion of sediments, food or exposure to the water column. Lynch and Johnson (1982) studied availability of radiolabelled hexachlorobiphenyl (HCBP) to benthic amphipods from experimentally contaminated natural sediments. They found that organisms exposed to water and contaminated sediments had higher (from 2.3 to 10 times) concentrations than did organisms exposed only to water. Furthermore, they found that the ratio of total bioaccumulation to bioconcentration decreased with exposure time. This implied that the importance of food uptake decreased with exposure duration, and that the ultimate equilibrium state of the animal is independent of the uptake pathway.

Schnoor (1982) attempted to determine the applicability of laboratory-derived BCFs for predicting actual field BCFs for a variety of hydrophobic organic chemicals in fish. He concluded that field BCFs, when normalized on a lipid basis, were within a factor of 1 to 4 of laboratory-derived BCFs. He suggested that laboratory-derived BCFs could

be used in fate and effects modeling with order of magnitude accuracy, or better.

INTERPRETIVE FRAMEWORK FOR BENTHIC BIOACCUMULATION

In attempting to relate sediment exposure concentrations of organic chemicals to concentrations in benthic organisms and fish, two questions immediately arise. The first question concerns the validity of extending existing relationships between BCF and K_{ow} from pelagic animals to benthic animals. The second question concerns the characterization of phase partitioning of organic chemicals in the sediment. This issue arises because actual field data for interstitial water concentrations are virtually non-existent.

Following the arguments of Mackay (1982) that bioconcentration is a simple phase partitioning phenomenon, it seems reasonable to apply existing relationships between BCF and K_{ow} to benthic organisms and fish. The principal difficulty occurs in specification of an appropriate exposure concentration of the chemical in the interstitial water. In principle, equilibrium partition relationships could be used to estimate interstitial water concentrations from total bulk sediment concentrations and sediment solids concentration. However, the validity of conventional partitioning theory has been challenged and the entire area of phase partitioning of organic chemicals in bottom sediments is an unresolved research issue. This is discussed below in more detail. As a first approximation, the conventional theory of reversible equilibrium partitioning is assumed to be valid in the sediments.

Connor (1984) has suggested that chemical concentrations in benthic fish should be referenced to sediment concentrations instead of directly to aqueous phase concentrations. This approach assumes that fish and

sediments will be in equilibrium through their individual equilibria with the aqueous phase. This assumption is consistent with the theoretical arguments by Mackay (1982) on multi-phase equilibrium partitioning.

Connor originally developed a relationship for the fish/sediment ratio of a chemical in terms of K_{ow} and the fraction organic carbon (f_{oc}) in the sediment. This relationship was based on a combination of two regression equations developed by Kenaga and Goring (1980) for BCF and sediment partition coefficient (K_{sed}). Connor (1985) proposed that regression equations developed by Mackay (1982) for fish BCF, and by Karickhoff et al. (1979) for organic chemical phase partitioning, be combined to yield the following expression for fish/sediment ratio:

$$\frac{BCF}{K_{sed}} = \frac{0.076}{f_{oc}} \qquad (1)$$

Dimensionally, the ratio BCF/K_{sed} is equivalent to the ratio of chemical concentration in fish (wet weight) to chemical concentration in sediment (dry weight). This equation has appeal because of its simplicity and because it contains no explicit dependence on K_{ow} or on interstitial water concentration.

An important assumption in the Mackay-Karickhoff equation is that phase partitioning of organic chemicals in the sediment follows the relationship developed by Karickhoff et al. (1979) for more dilute suspensions. In particular, potential complications due to the effects of solids concentrations on equilibrium partition coefficients and to colloidal phases are not explicitly addressed. These are discussed below in more detail.

The predictions of animal/sediment concentration ratio from the Mackay-Karickhoff equation are illustrated in Fig. 5.4. Consistent with

the definition of bioconcentration, and with the assumptions of the two component regression equations, this relationship provides a conservative estimate of actual environmental residues in benthic organisms and fish. Furthermore, it provides an approximate criterion for determining whether biomagnification may be contributing to observed accumulation levels.

FIELD DATA FOR BENTHIC BIOACCUMULATION

This section contains an examination of available field data for animal/sediment concentration ratios of organic chemicals in benthic organisms and fish. The objectives of this analysis are to determine if actual residue values are consistent with the simplified theory underlying the Mackay-Karickhoff equation and to determine whether biomagnification might be occurring.

Field data for chlorobenzenes, PCBs and hexachlorobutadiene (HCBD) in Lake Ontario oligochaetes and amphipods have been reported by Fox et al. (1983) (Figs. 5.5 and 5.6). The oligochaetes were primarily *Tubifex tubifex* and the amphipods were primarily *Pontoporeia hoyi*. Reported animal concentration data were converted from dry to wet weight by assuming that dry weight was 15% of wet weight (Oliver 1984). The curve on each plot represents the predictions of the Mackay-Karickhoff equation.

In general, the higher ratios correspond to the more highly chlorinated chemicals. In particular, the highest values in each case correspond to hexachlorobenzene (HCB) and PCB. These have the highest K_{ow} values of the reported chemicals and they do not degrade significantly in the environment. The lower chlorobenzenes are thought to be metabolized by the benthic organisms and/or microbially degraded.

Although the amphipods tended to have higher ratios than the oligochaetes, results for both groups of organisms were reasonably

consistent with predictions from the simplified partitioning theory. Mackay (1982) reported a standard error of 1.8 BCF in his regression of BCF vs K_{ow}. Karickhoff et al. (1979) did not report the standard error for their regression of sediment partition coefficient vs K_{ow} ($r^2 = 0.96$). None of the oligochaete ratios, and only one of the amphipod ratios, exceed the Mackay-Karickhoff predictions by greater than a factor of 2.

It is possible that differences in feeding habits are responsible for the observed differences in chemical accumulation. Oligochaetes live within the surficial sediment and continuously ingest sediment particles. Amphipods are found at the sediment-water interface and deposit feed directly on detritus.

Data for PAHs in Lake Erie oligochaete worms and chironomid midges have been reported by Eadie et al. (1983b) (Figs. 5.7 and 5.8). The worms were primarily *Limnodrilus* and the midges were primarily *Chironomus* and *Procladius*. In general, the ratios for the worms and midges are consistent with the simplified theory. None of the worm ratios, and only two of the midge ratios, exceed the Mackay-Karickhoff predictions by greater than a factor of 2.

Data for PAHs in Lake Michigan *Pontoporeia* have also been reported by Eadie et al. (1983b) (Fig. 5.9). These ratios appear somewhat higher than the predictions of the simplified theory. Two of the four data points for $f_{oc} = 0.004$, and all six of the data points for $f_{oc} = 0.017$, exceed the Mackay-Karickhoff predictions by greater than a factor of 2. It is possible that biomagnification, as well as bioconcentration, are both contributing to the observed accumulation levels.

Data for PCBs in benthic fish have been summarized by Connor (1984) and are re-plotted in Fig. 5.10. These data are from ten separate studies

and they include a laboratory aquarium, six marine sites and three freshwater sites (one in Lake St. Clair and one in Lake Erie). The organic carbon content of the associated sediments was not reported in any of the studies. The curve on the plot represents the predictions of the Mackay-Karickhoff equation for f_{oc} = 0.01 (1 percent). These predictions are a reasonable upper bound from the simple theory because the actual f_{oc} values of the sediments were probably greater than 0.01, and because higher values of f_{oc} would correspond to lower predictions for the fish/sediment ratio.

Connor plotted the data as a function of flushing time because he postulated that a certain minimum water residence time might be required to ensure equilibrium conditions between sediments and fish. He speculated that the fish/sediment ratios appeared to plateau at flushing times greater than 100 days, suggesting that the time necessary for fish-sediment equilibrium in the field may be of the same order as in laboratory bioconcentration studies.

Apart from any possible relationship between fish-sediment concentration ratios and flushing time, there appears to be much scatter in the data. Furthermore, four of the ratios exceed the upper bound prediction of the Mackay-Karickhoff equation by greater than a factor of 2, and one of them exceeds this prediction by an order of magnitude. If this simplified partitioning theory is valid then it appears that biomagnification may account for a significant portion of the total accumulation of PCBs by benthic fish. Clearly, the limited data presented here are insufficient to resolve this important issue.

RELATIONSHIP BETWEEN BIOACCUMULATION AND SEDIMENT EXPOSURES

Two potential weaknesses in the theory underlying the simplified

Mackay-Karickhoff equation are lack of explicit dependence of K_{sed} on solids concentration and lack of consideration of potential colloidal phases. O'Connor and Connolly (1980) synthesized results from a large number of independent laboratory studies and demonstrated that an inverse relationship existed between equilibrium partition coefficients and the concentrations of adsorbing solids. Horzempa and DiToro (1983) found that although variations in solution chemical composition and kinetic effects influenced partitioning, neither factor appeared to completely account for the magnitude of the observed sediment concentration effect in their experiments.

The potential influence of suspended solids concentrations on partition coefficients is not limited to laboratory experiments. Capel and Eisenreich (1985) found an inverse log relationship between PCB partition coefficients and suspended solids concentrations in Lake Superior. This behavior was partially attributed to differences in organic carbon content of the particles in different regions of the lake and to artifacts in the filtration process used. Swackhamer and Armstrong (1987) found a similar relationship in Lake Michigan.

Some workers have explained the influence of solids concentration on partition coefficients in terms of "third phases". Voice et al. (1983) studied the sorption of four hydrophobic chemicals on three different sediments from Lake Michigan. They found significant increases in equilibrium partition coefficents as solids concentration decreased. They suggested that this phenomenon was caused by the presence of microparticulates contributed by the adsorbing solids and not removed from suspension in the separation procedure. Gschwend and Wu (1985) studied the sorption of several PCB isomers on bottom sediments from Lake Superior

and the Missouri River. They contended that if precautions are taken to eliminate or account for non-settling (or non-filterable) microparticulates or organic macromolecules which remain in the aqueous phase during laboratory experiments, then equilibrium partition coefficients will remain constant over a wide range in suspended solids concentration.

The potential association of hydrophobic organic chemicals with dissolved organic matter can also confound the interpretation of experimental sorption data. Hassett and Anderson (1979) reported that cholesterol could be bound by dissolved organic matter (DOM) and stabilized in the aqueous phase. Chiou et al. (1986) found significant enchancements in solubility due to association with DOM of soil and aquatic origins. They contended that this phenomenon could cause the apparent dependence of partition coefficients on sediment concentrations. Carter and Suffet (1982) suggested that a significant fraction of DDT in natural waters may be bound to dissolved humic material, and that this could cause an apparent particle concentration effect on equilibrium partition coefficients. Landrum et al. (1984) showed that the equilibrium partition coefficient for binding of a variety of hydrophobic chemicals to humic acid and dissolved organic carbon (DOC) in natural waters was inversely proportional to the concentration of DOC in solution.

The presence of colloidal phases may significantly affect the bioavailability of organic chemicals. Landrum et al. (1985) suggested that reduction in bioavailability in the presence of DOC may explain anomalies observed in predicting bioaccumulation of chemicals with log K_{ow} > 6 (e.g. Oliver 1984). He postulated that much higher proportions of high log K_{ow} chemicals would be complexed by DOC as compared to lower K_{ow}

chemicals. Complexation by DOC would tend to reduce the true aqueous phase concentration of the chemical. Landrum et al. (1987) demonstrated that DOM in actual interstitial waters from Lake Michigan sediments reduced the bioavailability of PAH and PCB to *Pontoporeia*.

If partition coefficients are, in fact, lower in the sediment than predicted by conventional partitioning theory (e.g., Karickhoff et al. 1979), then benthic organisms would be exposed to higher aqueous phase concentrations in the interstitial water than in the water column. Conversely, if partitioning to DOM/DOC is significant in the sediment, then higher interstitial water concentrations may not represent true aqueous phase concentrations. If only the true aqueous phase concentrations of organic chemicals are bioavailable, then these two phenomena may tend to oppose each other.

DiToro (1985) has proposed a mechanistic particle interaction model for the reversible component partition coefficient. He successfully applied this model to data for a large number of neutral hydrophobic organic chemicals. Figure 5.11 contains a comparison between the predictions of this model for PCB partition coefficient, and data for the water column (Eadie et al. 1983a) and sediments (Rice et al. 1983) in Lake Michigan. The data indicate that apparent partition coefficients are significantly lower in the sediments than in the water column. The model predictions agree with the data for the water column, but they are substantially lower than the data for the sediments. It is not possible to determine if the measured sediment partition coefficients were underestimated due to the presence of a non-separable third phase.

It is instructive to examine the relationship between concentrations of organic chemicals in benthic organisms and the corresponding

equilibrium aqueous phase concentrations. This approach has been used in the water column to estimate aqueous phase concentrations of DDT and PCBs from fish body burdens (Bierman and Swain 1982; Rodgers and Swain 1983). Figure 5.12 illustrates the hypothetical animal-water relationships for PCBs (log BCF = 5.15 from Mackay 1982) using the oligochaete and amphipod data from Lake Ontario, and the interstitial water concentration data from Lake Michigan.

Assuming that bioconcentration is the only process responsible for accumulation in the animals, results indicate that the oligochaetes and amphipods would be in equilibrium with aqueous phase concentrations of 1 to 20 ng/L. Conversely, under the same assumption, the interstitial pore water concentrations would result in animal concentrations of 10 to 100 ppm (wet weight) at equilibrium. Water column concentrations of PCBs in the Great Lakes range between 1 and 10 ng/L (e.g., Rice et al. 1983). Animal concentrations of PCBs generally do not exceed 10 ppm (wet weight) (Great Lakes Water Quality Board 1983).

These results imply that true aqueous concentrations in the interstitial water are not substantially different than aqueous concentrations in the water column, or that benthic organisms are in equilibrium with water column concentrations instead of sediment concentrations. Alternatively, if benthic organisms are at equilibrium with reported interstitial water concentrations, then these concentrations are not completely bioavailable.

UNRESOLVED RESEARCH ISSUES

There are many unresolved research issues in the area of organic chemical accumulation by benthic organisms and fish. Historically, much more emphasis has been placed on the pelagic food chain. Some of these

unresolved issues relate to the sediment exposure environment and others relate to the linkage between sediment exposures and bioaccumulation. Still other issues relate to the very structure of benthic food chains.

The major unresolved issues related to benthic food chains are:

1. The number and types of trophic linkages within the benthic food chain .
2. The number and types of linkages between the benthic and pelagic food chains.
3. Identification of the major carbon transport pathways through the benthic food chain.
4. Identification of the minimum number of feeding types and trophic compartments required to account for the majority of the carbon transport through the benthic food chain.

The major unresolved issues related to the sediment exposure environment are:

1. Characterization of chemical phase partitioning. Methods are needed for estimating interstitial water concentrations from bulk sediment properties that can be more easily measured.
2. Determination of the significance of colloidal phases and complexation to macromolecules.
3. Characterization of the bioavailable component of total sediment exposure concentrations.
4. Quantification of the physical-chemical alterations to the sediments by benthic organisms.
5. Determination of the significance of microbially-mediated degradation of organic chemicals in sediments.

Some of the major unresolved issues related to bioaccumulation by benthic organisms and benthic fish are:

1. Validity and limits of applicability of existing empirical correlations between bioconcentration factors and chemical exposure concentrations.
2. Potential improvements to simple empirical correlations by normalizing to lipid content or to other characteristic biological parameters.

3. Determination of ingestion, assimilation, metabolism and excretion rates of organic chemicals by benthic organisms and fish.

The single principal obstacle to understanding and describing organic chemical dynamics in benthic food chains is lack of adequate field data for sediment exposures and animal accumulation levels. Field data are required in order to make initial judgements on the appropriate degree of model complexity for benthic bioaccumulation and potential coupling to the pelagic food chain. Ultimately, field data provide the final test for different hypotheses on model structure and process mechanisms.

SUMMARY AND CONCLUSIONS

There is considerable uncertainty regarding the structure and function of the benthic food chains in the Great Lakes. Furthermore, potential coupling between the benthic and pelagic food chains is poorly understood.

Benthic organisms can have significant effects on the physical and chemical properties of sediments and on constituent mass fluxes across the sediment-water interface. Models for microscopic scale processes of sorption kinetics and equilibrium, and for exposure of bed particles to overlying waters are only in the early stages of development. Sediment pelletization may mitigate sediment mass fluxes by trapping sorbed chemicals and significantly retarding chemical release into the aqueous phase at the sediment-water interface.

Environmental contaminants can be accumulated by benthic organisms and fish through direct uptake from water and through food chain uptake. The primary mode of accumulation in a particular case depends on the properties of the chemical, the relative concentrations of the chemical in the water and food, and on the trophic position of the animal. Under certain conditions, octanol-water partition coefficients can be good predictors of bioconcentration factors in fish and benthic organisms.

These factors are only conservative estimates of actual environmental accumulation levels because these levels are the result of potential food uptake, as well as bioconcentration.

A simplified partitioning relationship was used to examine the available field data for animal/sediment concentration ratios of organic chemicals in benthic organisms and fish. Reported ratios for oligochaete worms in Lakes Ontario and Erie, and chironomid midges in Lake Erie, were consistent with biococentration due to simple phase partitioning. Reported ratios for amphipods in Lake Ontario were also consistent with simple phase partitioning, however, ratios for amphipods in Lake Michigan appeared to indicate that biomagnification may be important. Data for benthic fish were extremely limited, however, they appeared to indicate that biomagnification accounted for a significant portion of total PCB body burdens.

These preliminary results indicate that accumulation of organic chemicals in macrobenthic invertebrates may be approximated using empirical relationships for bioconcentration. However, the description of accumulation levels in benthic fish may require a mechanistic food chain modeling approach.

The possible dependence of phase partition coefficients on solids concentration and potential interferences from colloidal phases are major obstacles to the characterization of sediment exposures. The available data are extremely limited, however, they appear to indicate that partition coefficients for PCBs are significantly lower in the sediment than in the water column. This implies that benthic organisms are exposed to much higher aqueous phase concentrations in the interstitial water than pelagic organisms exposed to the water column. However, reported values

for organic chemical accumulation in benthic organisms are not consistent with substantially higher exposures, thus indicating that interstitial water concentrations may not be completely bioavailable.

The single major obstacle to understanding and describing organic chemical dynamics in benthic food chains is lack of adequate field data for sediment exposures and animal accumulation levels.

REFERENCES

Adams, W.J., Kimerle, R.A., and Mosher, R.G., (1985). "Aquatic Safety Assessment of Chemicals Sorbed to Sediments", In Aquatic Toxicology and Hazard Assessment: Seventh Symposium, R.D. Cardwell, R. Purdy and R.C. Bahner (eds.), American Society for Testing and Materials, ASTM STP 854, 429-453.

Bierman, V.J., Jr., and Swain, W.R., (1982). "Mass Balance Modeling of DDT Dynamics in Lakes Michigan and Superior", Environ. Sci. Technol. 16(9), 572-579.

Capel, P.D., and Eisenreich, S.J., (1985). PCBs in Lake Superior, 1978-1980, J. Great Lakes Res. 11(4), 447-461.

Carter, C.W., and Suffet, I.H., (1982). "Binding of DDT to Dissolved Humic Materials", Environ. Sci. Technol. 16(11), 735-740.

Chiou, C.T., (1985). "Partition Coefficients of Organic Compounds in Lipid-water Systems and Correlations with Fish Bioconcentration Factors", Environ. Sci. Technol. 19(1), 57-62.

Chiou, C.T., Malcolm, R.L., Brinton, T.I., and Kile, D.E., (1986). "Water Solubility Enhancement of Some Organic Pollutants and Pesticides by Dissolved Humic and Fulvic Acids", Environ. Sci. Technol. 20(5), 502-508.

Connor, M.S., (1984). "Fish/Sediment Concentration Ratios for Organic Compounds", Environ. Sci. Technol. 18(1), 31-35.

Connor, M.S., (1985). Reply to comment on "Fish/Sediment Concentration Ratios for Organic Compounds", Environ. Sci. Technol. 19(2), 199.

DiToro, D.M., (1985). "A Particle Interaction Model of Reversible Organic Chemical Sorption", Chemosphere 14(10), 1503-1538.

Eadie, B.J., Rice, C.P., and Frez, W.A., (1983a). "The Role of the Benthic Boundary in the Cycling of PCBs in the Great Lakes", In Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S.J. Eisenreich and M.S. Simmons (eds.), Ann Arbor Science Publishers, Ann Arbor, Michigan, 213-228.

Eadie, B.J., Robbins, J.A., Landrum, P.F., Rice, C.P., Simmons, M.S., McCormick, M.J., Eisenreich, S.J., Bell, G.L., Pickett, K.L., Johansen, K., Rossman, R., Hawley, N., and Voice, T., (1983b). "The Cycling of Toxic Organics in the Great Lakes: A 3-year Status Report", National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan, NOAA Technical Memorandum ERL GLERL-45, 163 p.

Flint, R.W., (1986). "Hypothesized Carbon Flow Through the Deepwater Lake Ontario Food Web", J. Great Lakes Res. 12(4), 344-354.

Fox, M.E., Carey, J.H., and Oliver, B.G., (1983). "Compartmental Distribution of Organochlorine Contaminants in the Niagara River and the Western Basin of Lake Ontario", J. Great Lakes Res. 9(2), 287-294.

Great Lakes Water Quality Board, (1983). "Report on Great Lakes Water Quality, Appendix on Great Lakes Surveillance", International Joint Commission, Windsor, Ontario.

Gschwend, P.M., and Wu, S., (1985). "On the Constancy of Sediment-water Partition Coefficients of Hydrophobic Organic Pollutants", Environ. Sci. Technol. 19(1), 90-96.

Gschwend, P.M., Wu, S., Madsen, O.S., Wilkin, J.L., Ambrose, R.B.Jr., and McCutcheon, S.C., (1986). "Modeling the Benthos-water Column Exchange of Hydrophobic Chemicals", U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia, 194 p.

Hassett, J.P., and Anderson, M.A., (1979). "Association of Hydrophobic Organic Compounds with Dissolved Organic Matter in Aquatic Systems", Environ. Sci. Technol. 13(12), 1526-1529.

Horzempa, L.M., and DiToro, D.M., (1983). "PCB Partitioning in Sediment-water Systems: The Effect of Sediment Concentration", J. Environ. Qual. 12(3), 373-380.

Karickhoff, S.W., Brown, D.S., and Scott, T.A., (1979). "Sorption of Hydrophobic Pollutants on Natural Sediments", Water Res. 13, 241-248.

Karickhoff, S.W., and Morris, K.R., (1985). "Impact of Tubificid Oligochaetes on Pollutant Transport in Bottom Sediments", Environ. Sci. Technol. 19(1), 51-56.

Kenaga, E.E., and Goring, C.A.I., (1980). "Relationship Between Water Solubility, Soil Sorption, Octanol-water Partitioning and Concentration of Chemicals in Biota", In Aquatic Toxicology: Proceedings of Third Symposium on Aquatic Toxicology, American Society for Testing and Materials, ASTM STP 707, 78-115.

Landrum, P.F., Nihart, S.R., Eadie, B.J., and Gardner, W.S., (1984). "Reverse-phase Separation Method for Determining Pollutant Binding to Aldrich Humic Acid and Dissolved Organic Carbon of Natural Waters", Environ. Sci. Technol. 18(3), 187-192.

Landrum, P.F., Reinhold, M.D., Nihart, S.R., and Eadie, B.J., (1985). "Predicting the Bioavailability of Organic Xenobiotics to *Pontoporeia hoyi* in the Presence of Humic and Fulvic Materials and Natural Dissolved Organic Matter", Environ. Toxicol. Chem. 4, 459–467.

Landrum, P.F., Nihart, S.R., Eadie, B.J., and Herche, L.R., (1987). "Reduction in Bioavailability of Organic Contaminants to the Amphipod *Pontoporeia hoyi* by Dissolved Organic Matter of Sediment Interstitial Waters", Environ. Toxicol. Chem. 6, 11–20.

Lee, H., II and Swartz, R.C., (1980). "Biological Processes Affecting the Distribution of Pollutants in Marine Sediments. Part II. Biodeposition and Bioturbation", In Contaminants and Sediments, Volume 2: Analysis, Chemistry, Biology, R.A. Baker (ed.), Ann Arbor Science Publishers, Ann Arbor, Michigan, 555–606.

Lynch, T.R., and Johnson, H.E., (1982). "Availability of a Hexachlorobiphenyl Isomer to Benthic Amphipods From Experimentally Contaminated Natural Sediments", In Aquatic Toxicology and Hazard Assessment: Fifth Conference, J.G. Pearson, R.B. Foster and W.E. Bishop (eds.), American Society for Testing and Materials, ASTM STP 766, 273–287.

Mackay, D., (1982). "Correlation of Bioconcentration Factors", Environ. Sci. Technol. 16(5), 274–278.

McCall, P.L., Tevesz, M.J.S., and Schwelgien, S.F., (1979). "Sediment Mixing by *Lampsilis radiata siliquoidea* (Mollusca) from Western Lake Erie", J. Great Lakes Res. 5(2), 105–111.

McCall, P.L., and Fisher, J.B., (1980). "Effects of Tubificid Oligochaetes on Physical and Chemical Properties of Lake Erie Sediments", In Aquatic Oligochaete Biology, R.O. Brinkhurst and D.G. Cook (eds.), Plenum Press, New York, 253–317.

McCall, P.L., and Tevesz, M.J.S., (1982). "The Effects of Benthos on Physical Properties of Freshwater Sediments", In Animal-Sediment Relations, P.L. McCall and M.J.S. Tevesz (eds.), Plenum Press, New York, 105–176.

Neely, W.B., Branson, D.R., and Blau, G.E., (1974). "The Use of the Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish", Environ. Sci. Technol. 8, 1113–1115.

O'Connor, D.J., and Connolly, J.P., (1980). "The Effect of Concentration of Adsorbing Solids on the Partition Coefficient", Water Res. 14, 1517–1523.

Oliver, B.G., and Niimi, A.J., (1983). "Bioconcentration of Chlorobenzenes From Water by Rainbow Trout: Correlations with Partition Coefficients and Environmental Residues", Environ. Sci. Technol. 17(5), 287–291.

Oliver, B.G., (1984). "Uptake of Chlorinated Organics From Anthropogenically Contaminated Sediments by Oligochaete Worms", Can. J. Fish. Aquat. Sci. 41, 878–883.

Oliver, B.G., and Niimi, A.J., (1987). "Trophodynamic Analysis of PCB Congeners and Other Chlorinated Hydrocarbons in the Lake Ontario Ecosystem", Accepted for publication in Environ. Sci. Technol.

Rice, C.P., Meyers, P.A., and Brown, G.S., (1983). "Role of Surface Microlayers in the Air–water Exchange of PCBs", In Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S.J. Eisenreich and M.S. Simmons (eds.), Ann Arbor Science Publishers, Ann Arbor, Michigan, 157–179.

Robbins, J.A., (1986). "A Model for Particle–selective Transport of Tracers in Sediments With Conveyor Belt Deposit Feeders", J. Geophys. Res. 91(C7), 8542–8558.

Rodgers, P.W., and Swain, W.R., (1983). "Analysis of Polychlorinated Biphenyl (PCB) Loading Trends in Lake Michigan", J. Great Lakes Res. 9(4), 548–558.

Schnoor, J.L., (1982). "Field Validation of Water Quality Criteria for Hydrophobic Pollutants", In Aquatic Toxicology and Hazard Assessment: Fifth Conference, J.G. Pearson, R.B. Foster and W.E. Bishop (eds.), American Society for Testing and Materials, ASTM STP 766, 302–315.

Swackhamer, D.L., and Armstrong, D.E., (1987). "Distribution and Characterization of PCBs in Lake Michigan Water", J. Great Lakes Res. 13(1), 24–36.

Thomann, R.V., and Connolly, J.P., (1984). "Model of PCB in the Lake Michigan Lake Trout Food Chain", Environ. Sci. Technol. 18(2), 65–71.

Veith, G.D., DeFoe, D.L., and Bergstedt, B.V., (1979). "Measuring and Estimating the Bioconcentration Factor of Chemicals in Fish", J. Fish Res. Board Can. 36, 1040–1048.

Voice, T.C., Rice, C.P., and Weber, W.J. Jr., (1983). "Effect of Solids Concentration on the Sorptive Partitioning of Hydrophobic Pollutants in Aquatic Systems", Environ. Sci. Technol. 17(9), 513–518.

FIGURE CAPTIONS

Fig. 5.1. Hypothesized trophic links in the Lake Ontario deepwater food web. Percentages suggest proportional contribution of food from various sources to trophic compartment (Flint, 1986).

Fig. 5.2. Theoretical model of an annual carbon production and energy flow food web for the deepwater habitat of Lake Ontario. All compartment production and carbon flow values are represented in g $C/m^2/yr$ (Flint, 1986).

Fig. 5.3. Simplified food chain for Lake Ontario (Oliver and Niimi, 1987).

Fig. 5.4. Predicted relationship between animal/sediment concentration ratio for organic chemicals and fraction sediment organic carbon using the Mackay-Karickhoff equation (see text).

Fig. 5.5. Organochlorine contaminants in Lake Ontario oligochaetes. data from Fox et al. (1983). Curve is predicted animal/sediment ratio from Mackay–Karickhoff equation (see text).

Fig. 5.6. Organochlorine contaminants in Lake Ontario amphipods. Data from Fox et al. (1983). Curve is predicted animal/sediment ratio from Mackay–Karickhoff equation (see text).

Fig. 5.7. Polyaromatic hydrocarbons (PAHs) in Lake Erie worms. Data from Eadie et al. (1983b). Curve is predicted animal/sediment ratio from Mackay–Karickhoff equation (see text).

Fig. 5.8. Polyaromatic hydrocarbons (PAHs) in Lake Erie midges. Data from Eadie et al. (1983b). Curve is predicted animal/sediment ratio from Mackay–Karickhoff equation (see text).

Fig. 5.9. Polyaromatic hydrocarbons (PAHs) in Lake Michigan *Pontoporeia*. Data from Eadie et al. (1983b). Curve is predicted animal/sediment ratio from Mackay–Karickhoff equation (see text).

Fig. 5.10. Total polychlorinated biphenyls (PCBs) in benthic fish. Data from Connor (1984). Curve is predicted animal/sediment ratio from Mackay–Karickhoff equation (see text) for 1% sediment organic carbon.

Fig. 5.11. Partition coefficient for PCBs as a function of solids Concentration. Data for total PCBs in water column (W) for Lake Michigan from Rice et al. (1983); Data for total PCBs in sediment (S) for Lake Michigan from Eadie et al (1983a). Curve is predicted partion coefficient for hexachlorobiphenyl from DiToro (1985).

Fig. 5.12. Hypothetical animal-water equilibrium relationships for total PCBs. Log BCF = 5.15 from Mackay (1982). Oligochaete (O) and amphipod (A) PCB concentrations from Fox et al. (1983) for Lake Ontario. Pore Water PCB concentrations (P) from Eadie et al. (1983a) for Lake Michigan.

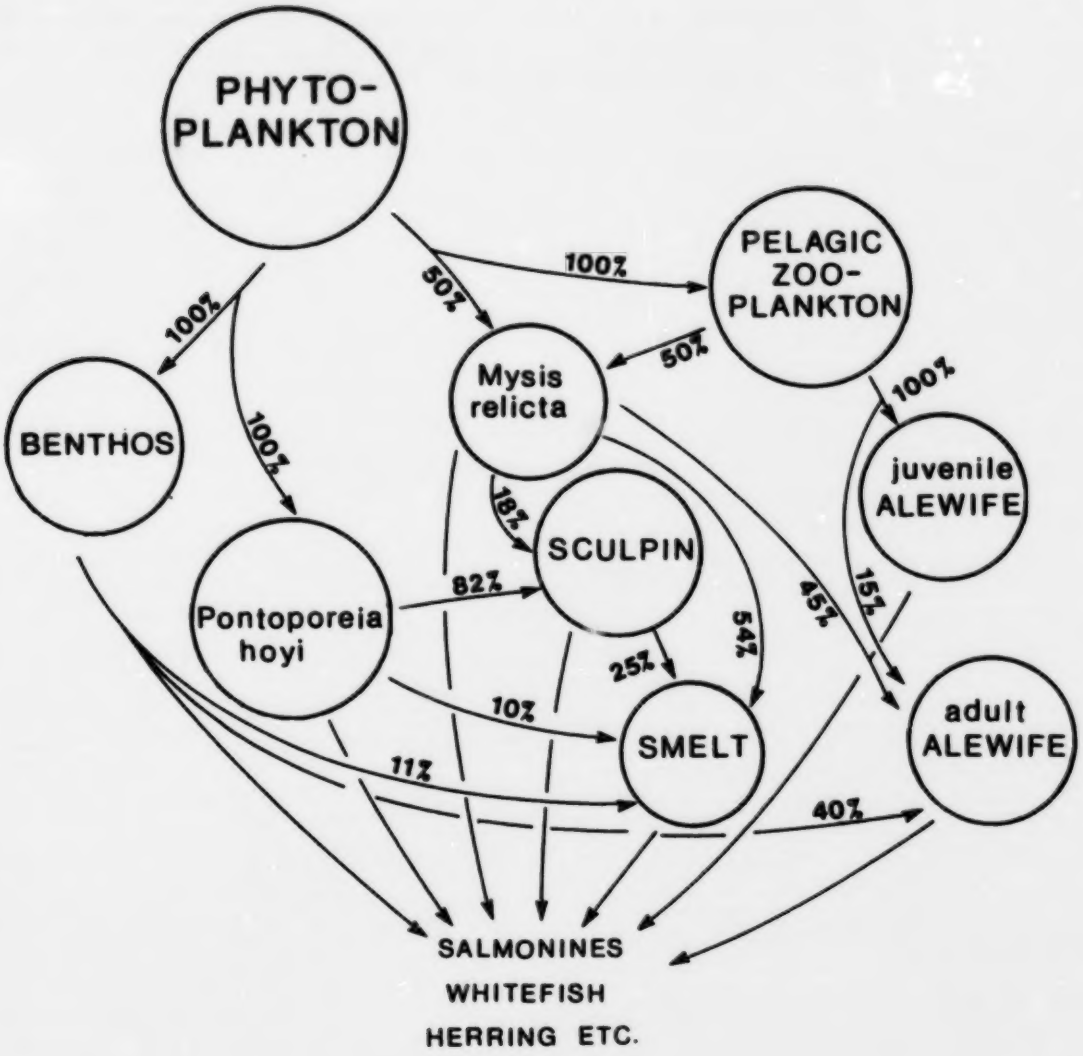

FIGURE 5.1: Hypothesized trophic links in the Lake Ontario deepwater food web. Percentages suggest proportional contribution of food from various sources to trophic component. (Flint, 1986)

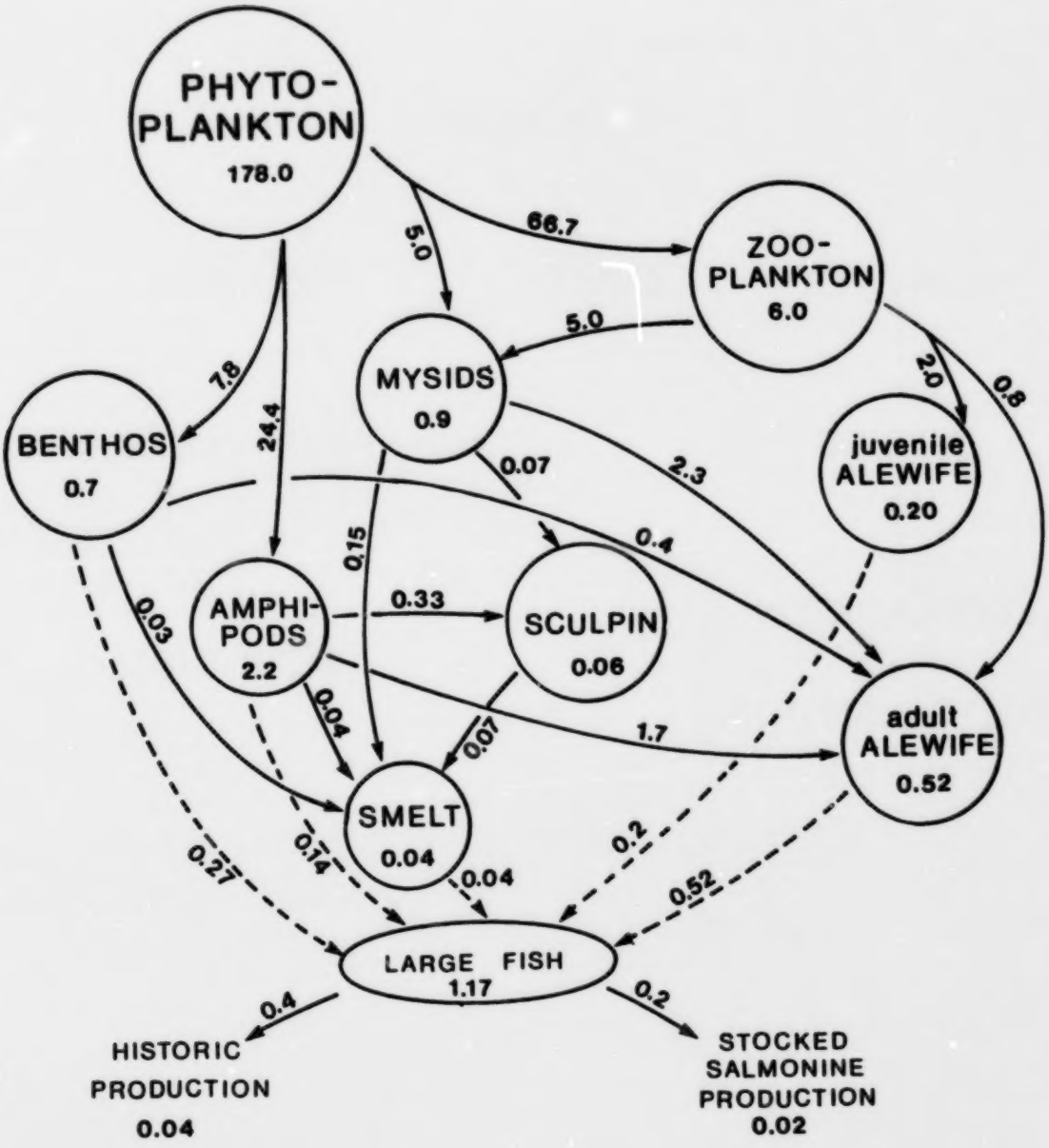

FIGURE 5.2: Theoretical model of an annual carbon production and energy flow food web for the deepwater habitat of Lake Ontario. All compartment production and carbon flow values are represented in g $C/m^2/yr$.

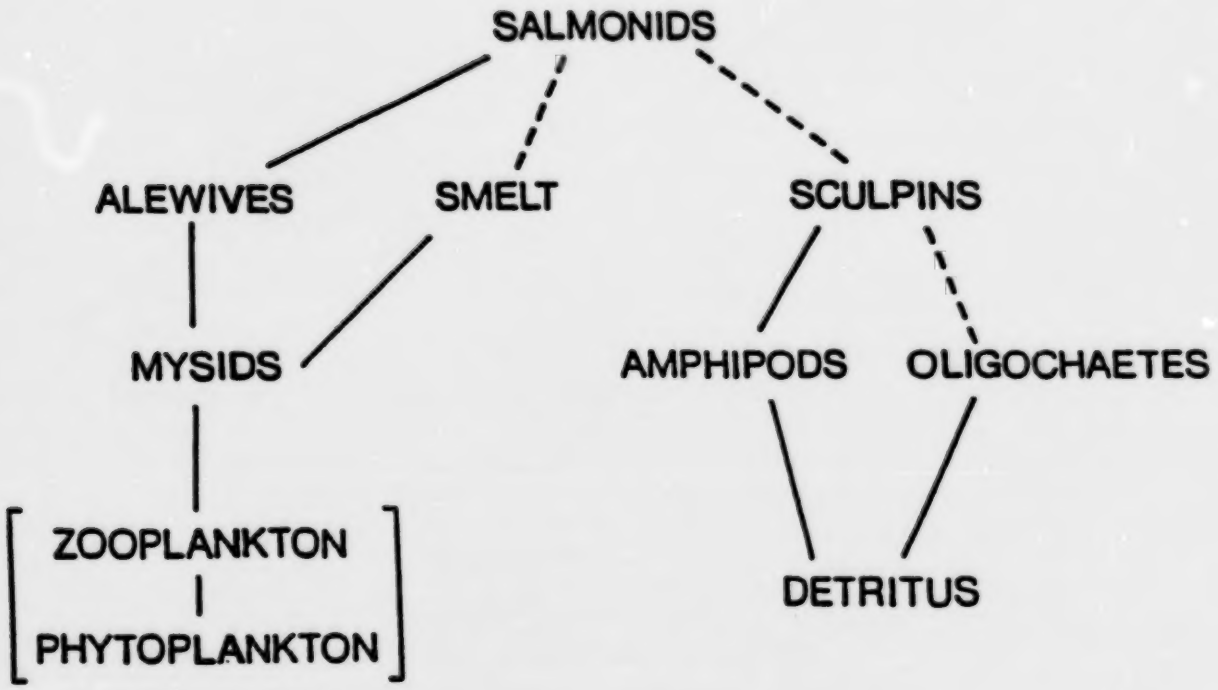

Figure 5.3

Simplified food chain for Lake Ontario (Oliver and Niimi 1987).

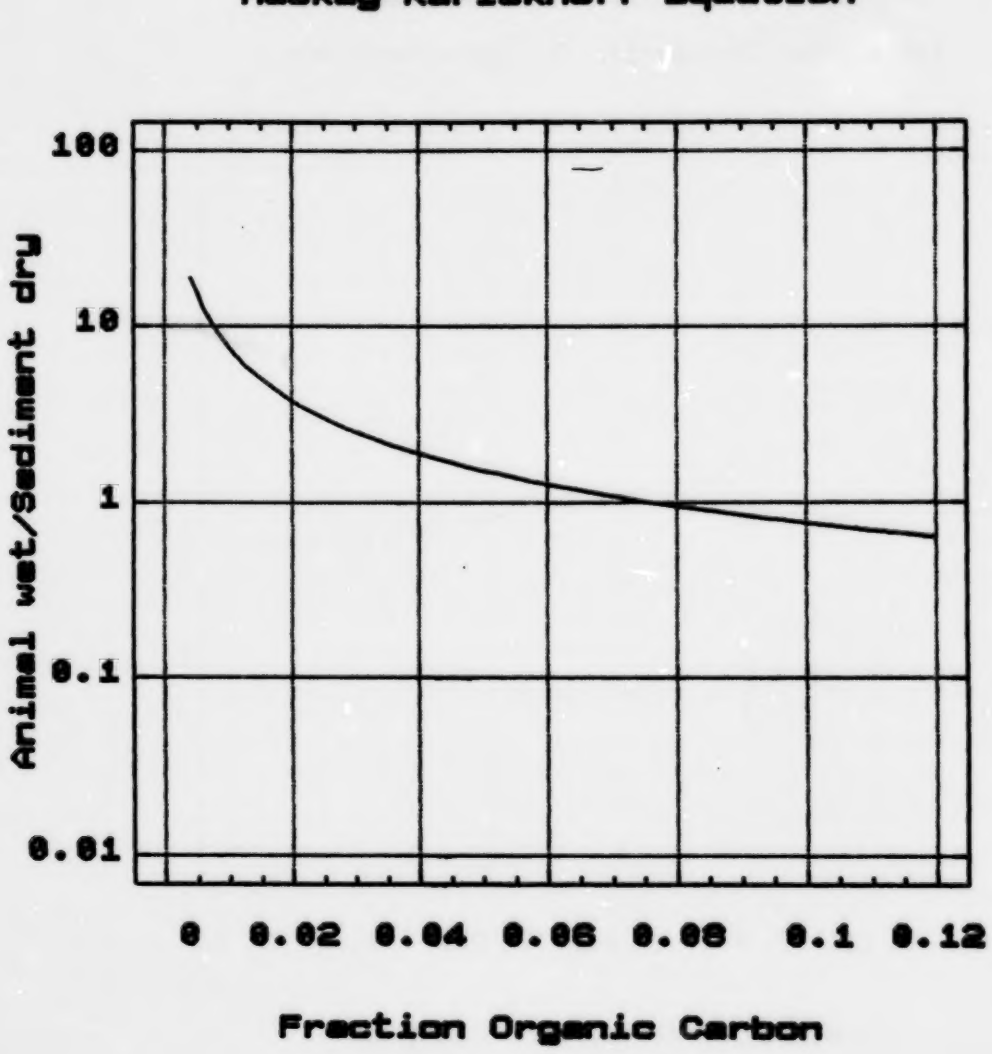

Fig. 5.4. Predicted relationship between animal/sediment concentration ratio for organic chemicals and fraction sediment organic carbon using the Mackay-Karickhoff equation (see text).

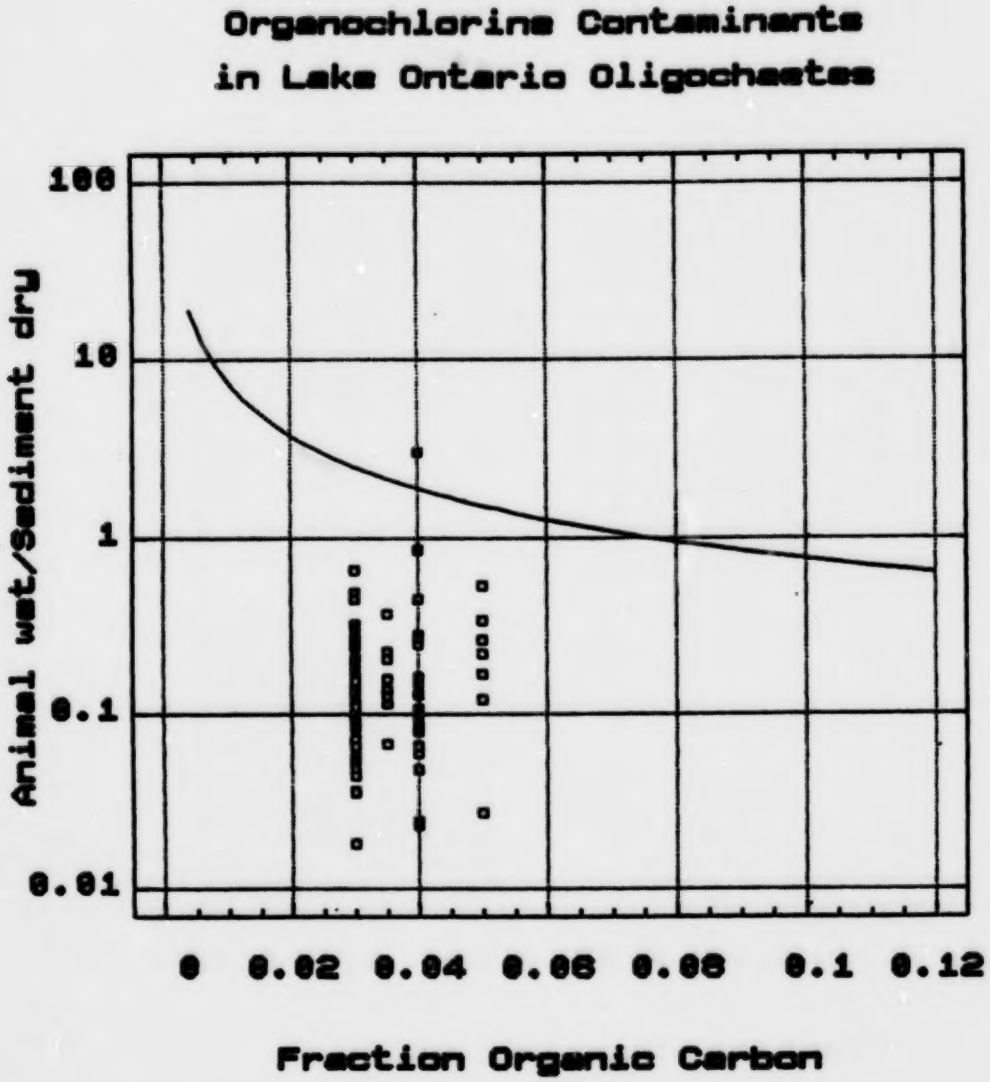

Fig. 5.5. Organochlorine contaminants in Lake Ontario oligochaetes. data from Fox et al. (1983). Curve is predicted animal/sediment ratio from Mackay-Karickhoff equation (see text).

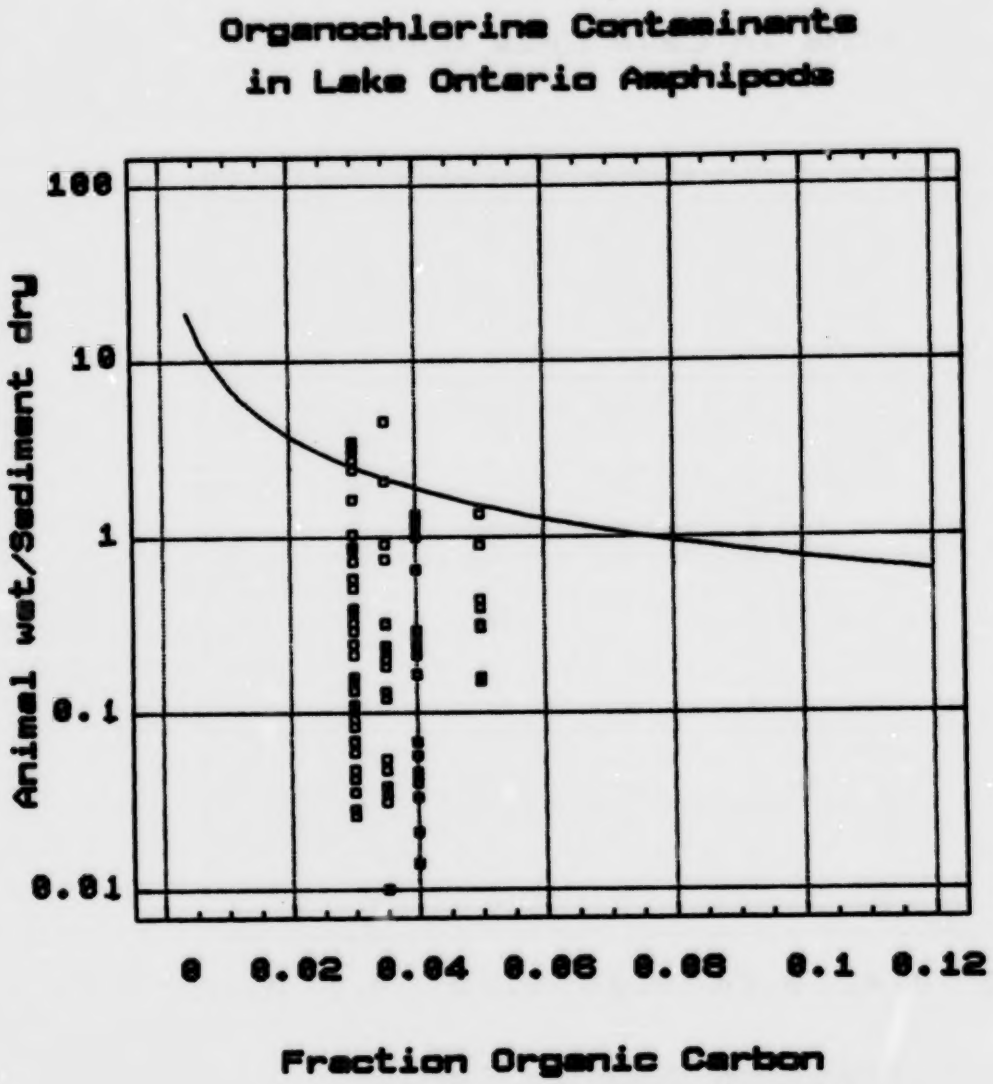

Fig. 5.6. Organochlorine contaminants in Lake Ontario amphipods. Data from Fox et al. (1983). Curve is predicted animal/sediment ratio from Mackay–Karickhoff equation (see text).

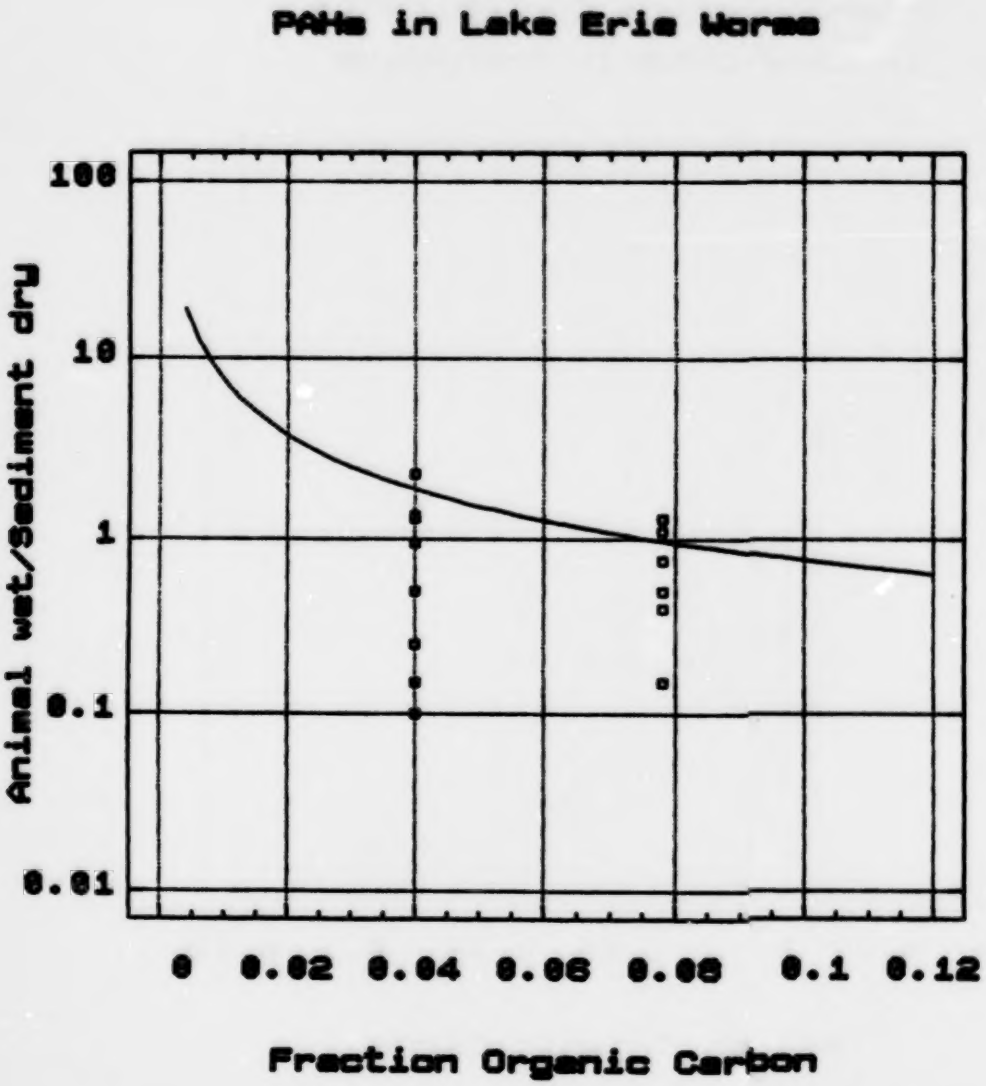

Fig. 5.7. Polyaromatic hydrocarbons (PAHs) in Lake Erie worms. Data from Eadie et al. (1983b). Curve is predicted animal/sediment ratio from Mackay-Karickhoff equation (see text).

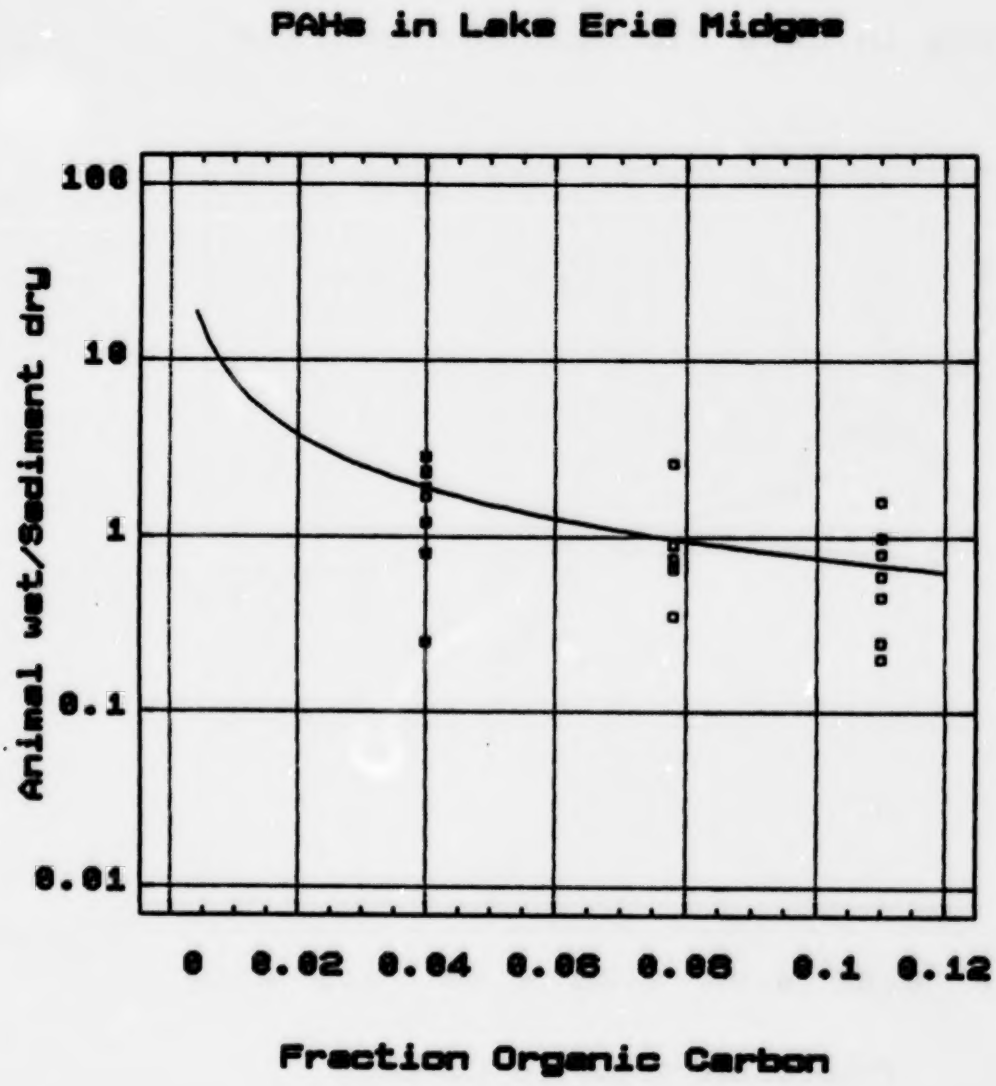

Fig. 5.8. Polyaromatic hydrocarbons (PAHs) in Lake Erie midges. Data from Eadie et al. (1983b). Curve is - predicted animal/sediment ratio from Mackay-Karickhoff equation (see text).

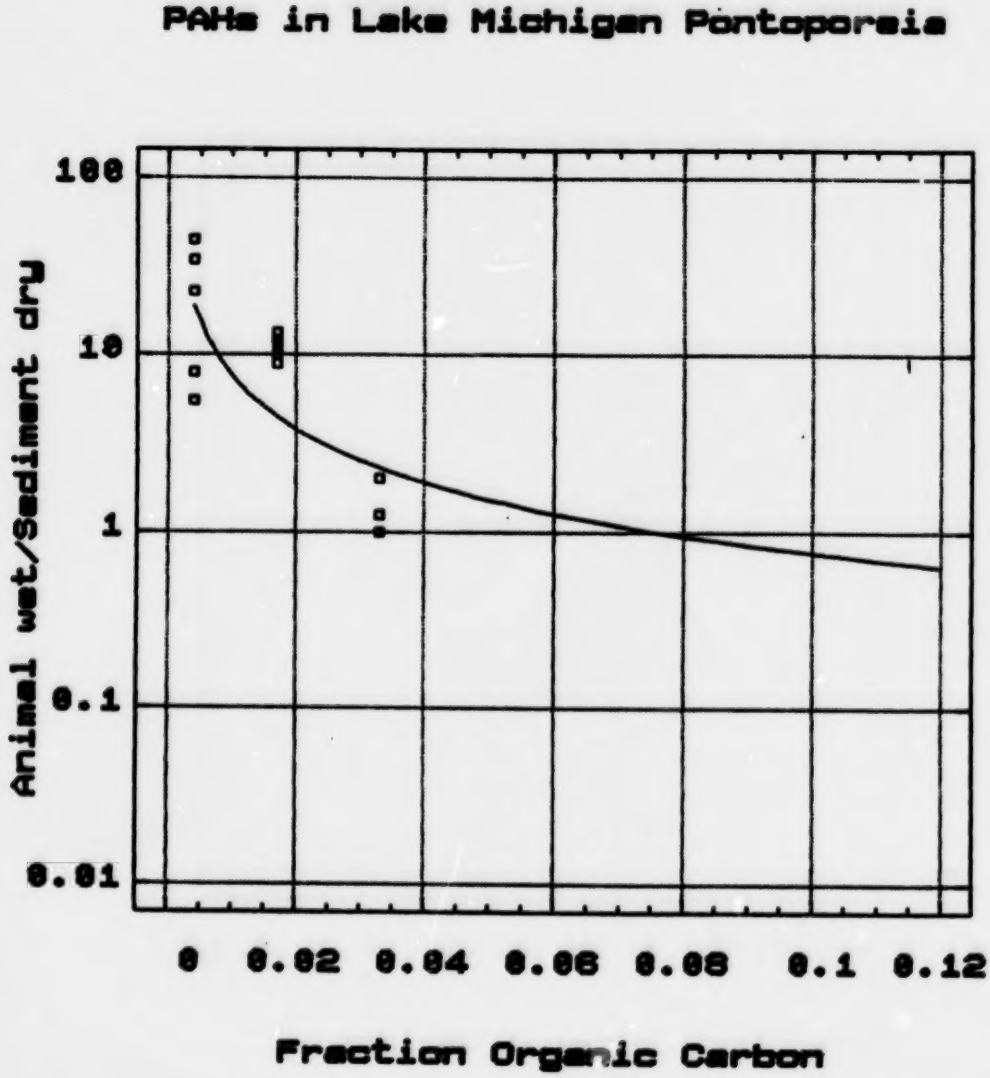

Fig. 5.9. Polyaromatic hydrocarbons (PAHs) in Lake Michigan *Pontopereia*. Data from Eadie et al. (1983b). Curve is predicted animal/sediment ratio from Mackay-Karickhoff equation (see text).

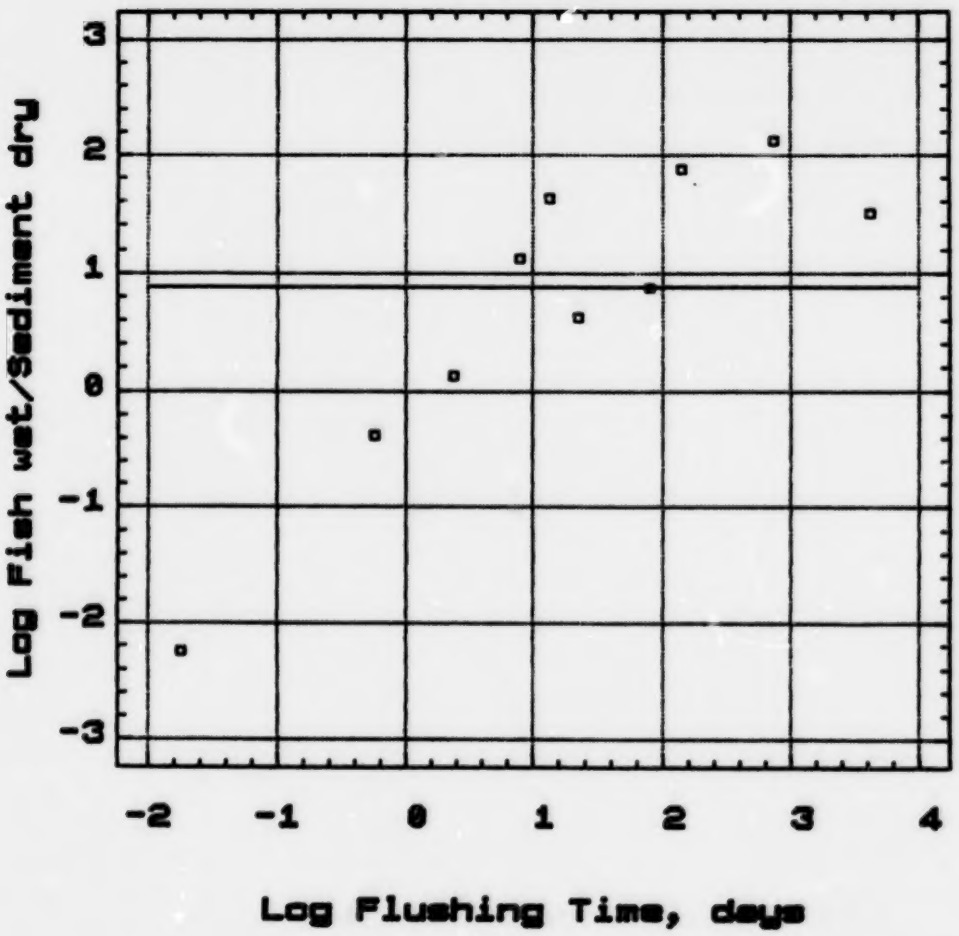

Fig. 5.10. Total polychlorinated biphenyls (PCBs) in benthic fish. Data from Connor (1984). Curve is predicted animal/sediment ratio from Mackay-Karickhoff equation (see text) for 1% sediment organic carbon.

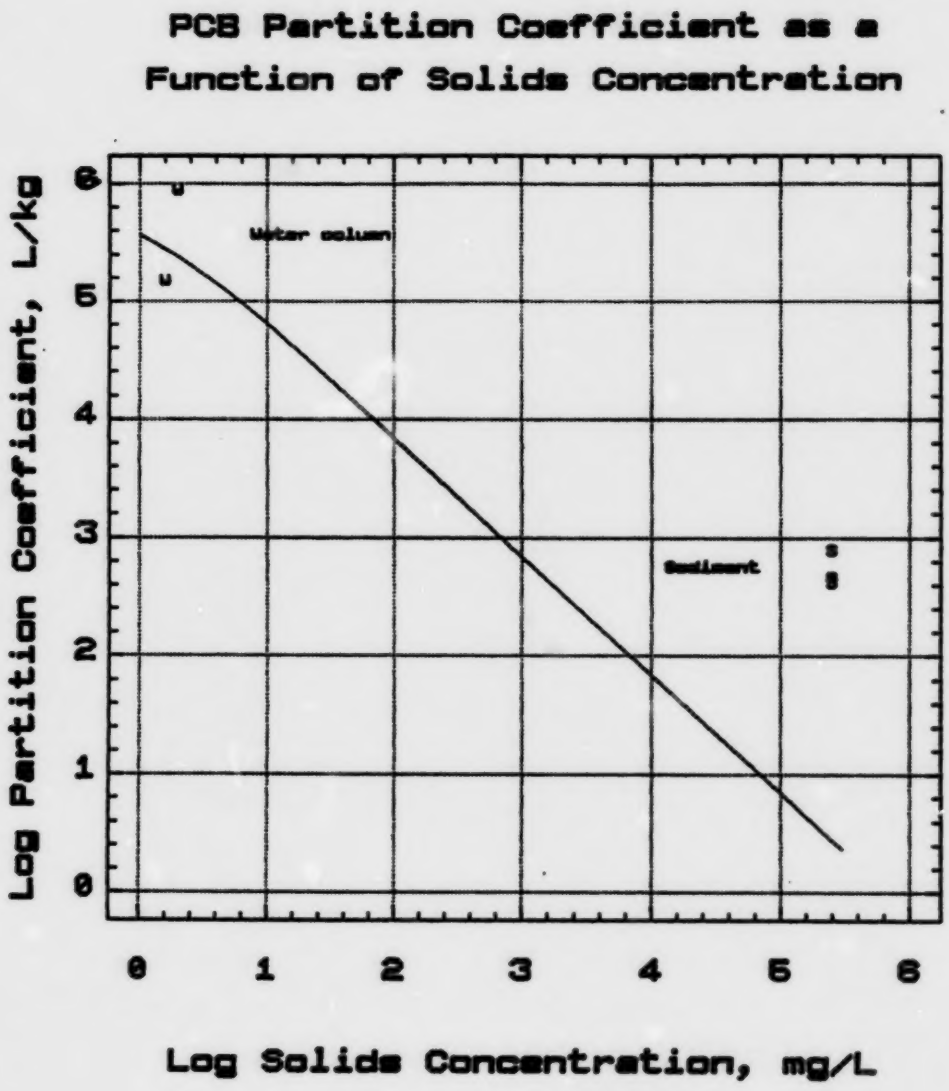

Fig. 5.11. Partition coefficient for PCBs as a function of solids Concentration. Data for total PCBs in water column (W) for Lake Michigan from Rice et al. (1983); Data for total PCBs in sediment (S) for Lake Michigan from Eadie et al (1983a). Curve is predicted partion coefficient for hexachlorobiphenyl from DiToro (1985).

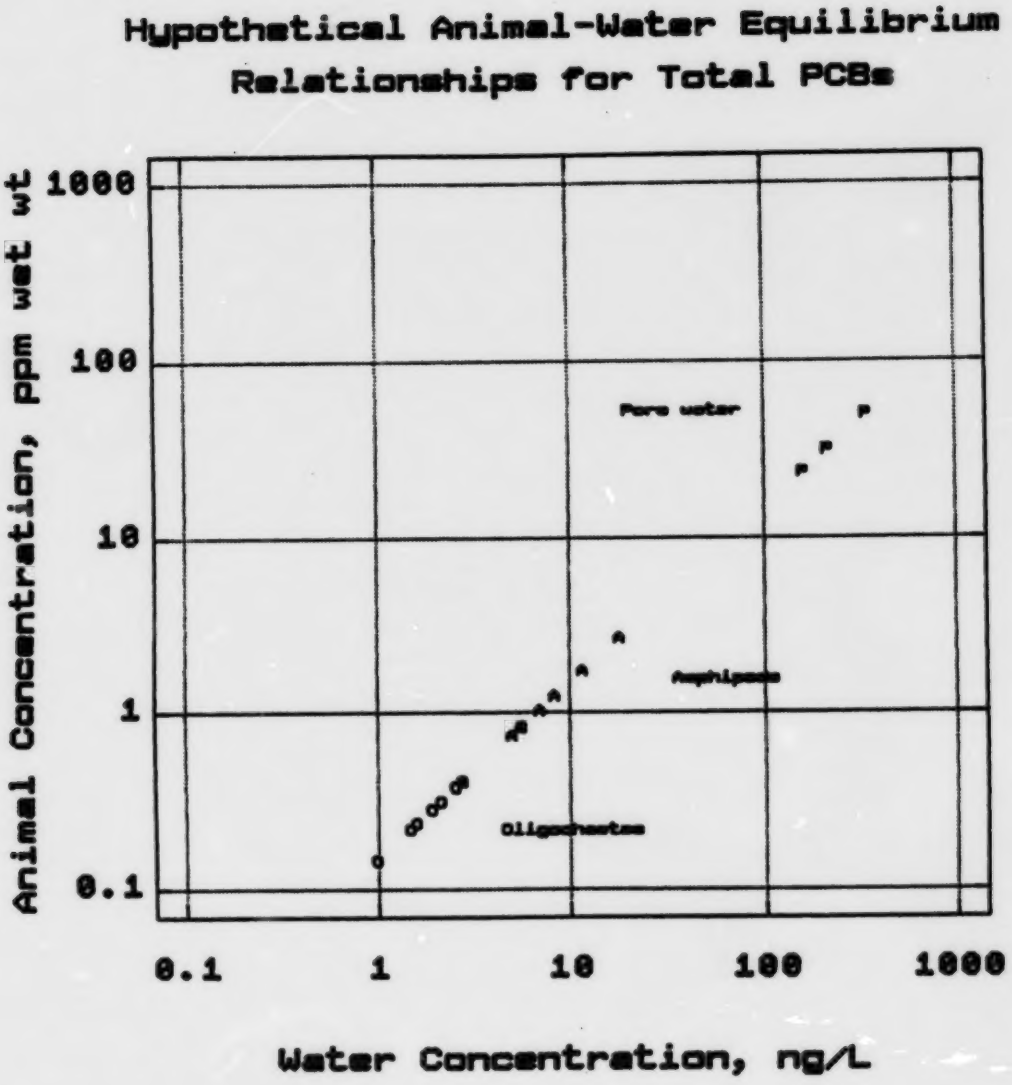

Fig. 5.12. Hypothetical animal-water equilibrium relationships for total PCBs. Log BCF = 5.15 from Mackay (1982). Oligochaete (O) and amphipod (A) PCB concentrations from Fox et al. (1983) for Lake Ontario. Pore Water PCB concentrations (P) from Eadie et al. (1983a) for Lake Michigan.

CHAPTER 6

FEEDING RELATIONSHIPS AND CONTAMINANT PATHWAYS PART I

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INTRODUCTION

To consider feeding relationships in biological systems one must recognize that biological systems are often built upon the concepts that energy must be transferred efficiently from one trophic level to another, and that the systems must also be stable over time and space. Long food chains are inherently unstable. They represent the most efficient pathway to transfer energy and therefore contaminants from the primary producers to the top predator. Simple food chains however require such close synchrony that any unusual event can interrupt the energy flow such that the resources at the upper level of the food chain can be seriously depleted. Resource managers in the past have given us prime examples as to what happens to ecological systems when food chain models have been selected to manage natural resources. Fisheries at one time spoke of maximum sustainable yield, and of course now speak of restoration and rehabilitation. The agricultural business selected plants for their fast growing abilities not for their resistance to disease or insects, thus our ever growing dependence on pesticides and fungicides. To consider feeding relationships one must consider food web models, and the positions of species within the food web. These are naturally much more complex, but still a great deal can be gained by looking at food webs as an integral part of environmental resource management.

FOOD WEBS

Let us first of all look at a generalized food web, and the properties one must consider of a food web. The first property is that the number of trophic levels that can be sustained in a food web are not a simple function of total energy flow. Indeed there appears to be a paradox in that a diversity of species is essential to develop a stable, multi-tiered

food web. This diversity of species obviously has an energy cost to maintain the interactive and interdependent relationships of species that comprise the food web. Energy spent in this manner is not available at other trophic levels, thus there is an energy cost for stability in food webs.

Stability in ecological systems is probably one of the most controversial areas one can enter, yet one cannot discuss ecological systems without recognizing there is a stability, i.e. we do recognize pattern in ecological systems. Some researchers such as Cairns and Van der Schalie consider there to be an "ecosystem assimilation" potential for dealing with (i.e. tolerating) the direct effects of toxic substances. To avoid some of the confusion associated with the word "stability" it is often better to consider two separate attributes of stability. The first is "perseverance" or the fact that food webs and ecosystems tend to conserve the number of species of which they are composed. The maximum number of potential links amongst all the species is given by

$$n = \frac{n\ (n - 1)}{2}$$

One of the better reviews of food webs with respect to perseverance is that of Briand (1980) who studied numerous terrestrial and aquatic food webs and concluded one could possibly develop a matrix to illustrate the connectance of species within a food web. It is probably not wise to generalize that the species with the greater number of connections are more important than those with less, but the loss of species with the greater number if interactions can possibly have a more profound effect on the long term stability of the food web. Should such species be physiologically more susceptible to the exposure of toxic substances, one would have to question what Cairns and Van der Schalie meant when

discussing "ecosystem assimilation capabilities". The loss of species to a food web undermines the stability of that food web, and there are good ecological reasons why environmental managers should return to the old concept of protecting the most sensitive species.

The second property of stability is probably well recognized by those who frequently discuss "food chain" dynamics, for it is closely related to the transfer of energy from one trophic level to another. This is the "constancy" of populations within an ecodeme. It is not surprising to see the number of discussions being held today on the Great Lakes ecosystem as to whether food chains are controlled from the top down or from the bottom up. I would like to propose today a comprise between food webbers and food chainers but unfortunately, ecology does not lend itself to compromise. Constancy and perseverance tend to result in very different management options. It is quite different to regulate or maximize the abundance of key economic species, than to try to maintain the diversity of the food web to which that species belongs.

Another important aspect not captured in the food chain concept is that there are many different associations that can exist among species. For example in Fig. 6.1 we can see that predation is only part of the species interactions found within a food web, and that these relationshps can have profound effects on energy flow or material transfer within an ecodeme. Other relationships such as competition, amensalism, parasitism, neutralism, commensalism, and mutualism should also be considered as such interactions help determine the structure and function of food webs, yet are ignored within the discussion of simple food chains.

FOOD WEB MODELLING

When attempting to model ecosystems, one is essentially trying to determine energy flows, recognizing that although we often draw energy "loops", energy is continually lost as heat, friction and advective transport of material out of the food web (e.g. loss of organic carbon to the deep sediments). Therefore when one is confronted with food web diagrams or models, one must first of all realize that what is being modelled is often not species interactions or interdependencies, but is essentially an energy budget. In order to model a representative energy budget for a food web one has to have measurements of the rate limiting steps illustrated in Fig. 6.2.

Factors that control the size and shape of the energy budget are:

$$\text{Ecological efficiency} = \frac{P_x}{P_{x+1}}$$

where P_x is the production at trophic level x

$$\text{Exploitation efficiency} = \frac{I_x}{P_{x+1}}$$

where I_x is the ingested portion at trophic level x

$$\text{Assimilation efficiency} = \frac{A_x}{I_{x+1}}$$

where A_x is the assimilated portion of food ingested

$$\text{Net production efficiency} = \frac{P_x}{A_x}$$

$$\text{Gross production} = I_x - E_x$$

where E_x is the excretory loss at trophic level x

Net production = G.P. (gross production) minus R_x (respiratory loss) at trophic level x.

One cannot look at such a list and not observe how important the word "efficiency" is. For example, assimilation efficiency varies in the

literature for different species from 15% to 90%. As there is a finite amount of energy entering the system and ecological efficiency is low, the number of trophic levels in a food web are limited. As mentioned earlier, ecological efficiency must compensate somewhat for system stability.

This limited number of trophic levels gave rise to the concept of the Eltonian pyramid, yet these can be quite different in terrestrial and aquatic systems Fig. 6.3. The production biomass ratio for terrestrial systems is much smaller than that for aquatic systems, and the length of the subsequent "food chain" in aquatic systems is frequently longer than that in terrestrial ecosystems.

The problem with Fig. 6.3, however, is that it tends to imply that energy can move only to the adjacent trophic level (steps cannot be skipped). Often however, as steps are skipped, and combined with the transfer of energy by detritivors into various tiers, one can see why ecological efficiency is very difficult to measure. This is an obvious area requiring more research if models of energy or contaminants can meet Levins (1960) criteria of being precise, general and realistic. Whether a heuristic model with driving processes as shown in Fig. 6.2 can simulate ecological systems in a realistic and precise manner remains to be seen. Interestingly, despite the need for such knowledge, this tends to be one of the poorest funded research areas simply because one must produce a monograph as opposed to a series of related papers.

FOOD WEB DYNAMICS AND CONTAMINANTS

The factors regulating food web models noted in Fig. 6.2, are essential for modelling contaminants, partitioning and concentrations in the food web. Contaminant burdens are measured often with regard to the ratio of contaminant mass to biological mass. If there is rapid recycling

of the biological mass in aquatic systems as observed in Fig. 6.3, and as the rate of recycling is decreased from one trophic level to the next there is an obvious problem in representing contaminant information in such a static fashion. An exposure at higher trophic levels can result in higher body burdens than at lower trophic levels. Simple contaminant bioaccumulation models often ignore this fact, and may result in false estimates of contaminant transfer.

Other important aspects of contaminant transfer is prey selection, seasonality and life cycle changes. It is not surprising to observe that aquatic contaminant transfers are often regulated at this level of the phytoplankton. Despite very low body burdens, any mass balance model based on production and not standing stock would greatly effect the prediction of many food chain models (Flint 1986).

CONCLUSION

I would hesitate to recommend we try to model and monitor all compartments and the species within food webs (indeed, during their life cycle, many species can change compartments). I think we must start with a simple model before we can start making testable hypotheses as to the movement and accumulation of contaminants in food webs. Perhaps food webs or food chains are the wrong concept to be using especially for the Great Lakes ecosystem until some basic and long overdue research on primary productivity, zooplankton grazing and fish predation has been done. We have ignored these factors during the eutrophication issue only to end up having "top down or bottom up" food web workshops. It would appear that, unless environmental managers wish to end up in the same position again, we must finally start doing some basic ecological research in the Great Lakes ecosystem.

REFERENCES

Briad, F., (1983). "Environmental Control of Food Web Structure", Ecology, 64:253–263.

Cairns, J. Jr., and Van der Schalie (1980). "Biological Monitoring – Early Warning Systems", Wat. Res. 14:1179–1196.

Flint, R.W., (1986). "Hypothesized Carbon Flow Through the Deepwater Lake Ontario Food Web", J. Great Lakes Res. 12:244–354.

FIGURE CAPTIONS

Fig. 6.1. A summary of biological interactions that can regulate the relative abundance and composition of communities.

Fig. 6.2. Factors regulating energy flow, carbon flow and potentially contaminant flow in ecosystems.

P_x: Production in trophic level x

I_x: Amount ingested

A_x: Amount of energy assimilated

E_x: Amount of energy excreted

R_x: Amount of energy lost through respiration

x + 1: Next lower trophic level

Fig. 6.3. Energy flow models of terrestrial and aquatic ecosystems. Note the different production: biomass ratios as discussed in the text.

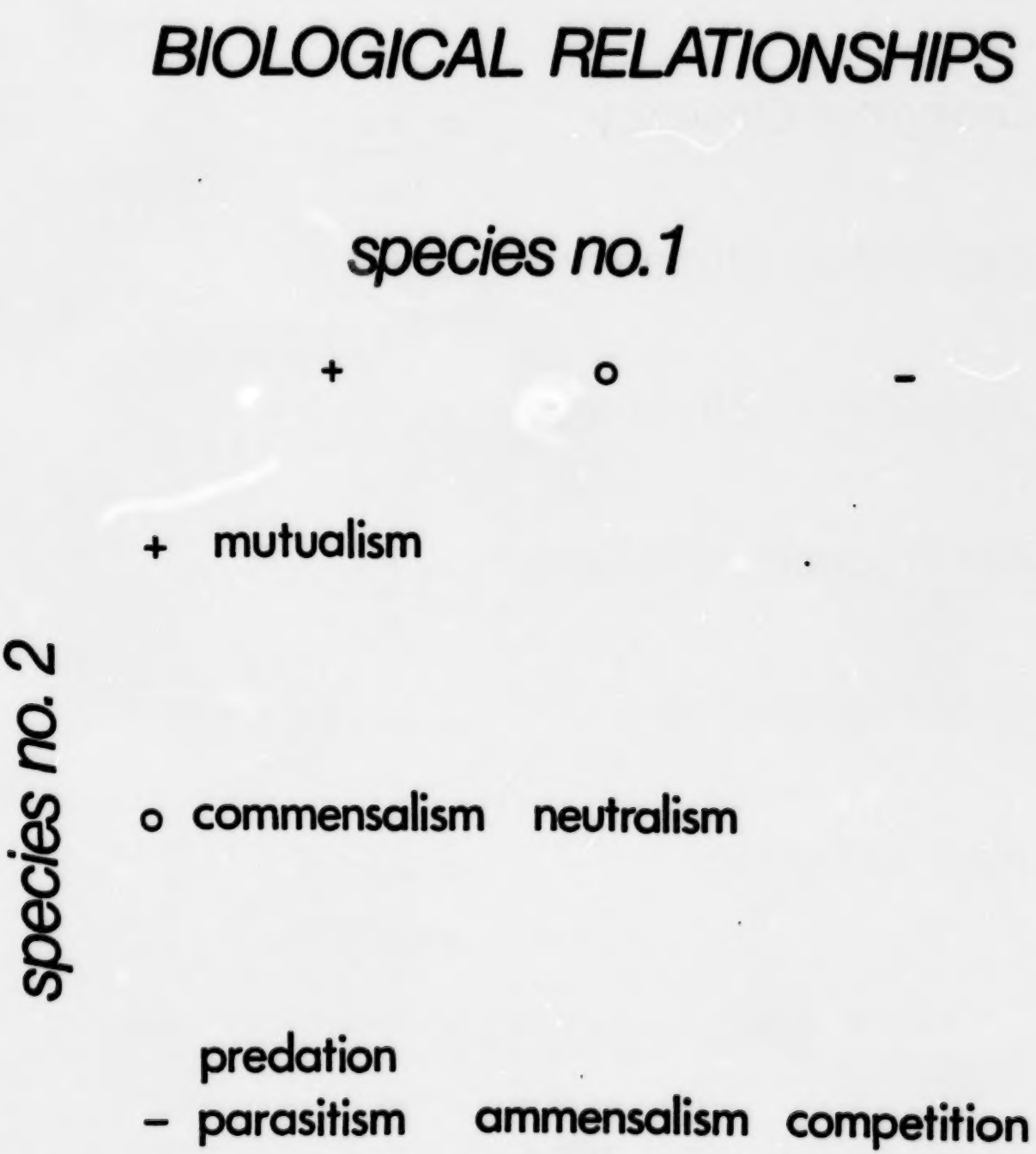

Figure 6.1: A summary of biological interactions that can regulate the relative abundance and composition of communities.

REGULATING FACTORS

$$\text{Ecological Efficiency} = \frac{P_x}{P_x + I}$$

$$\text{Exploitation Efficiency} = \frac{I_x}{P_x + I}$$

$$\text{Assimilation Efficiency} = \frac{A_x}{I_x}$$

$$\text{Net Production Efficiency} = \frac{P_x}{A_x}$$

$$\text{Gross Production} = I_x - E_x$$

$$\text{Net Production} = A_x - R_x$$

$$= G.P. - R_x$$

Fig. 6.2. Factors regulating energy flow, carbon flow and potentially contaminant flow in ecosystems.

P_x: Production in trophic level x

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$x + 1$: Next lower trophic level

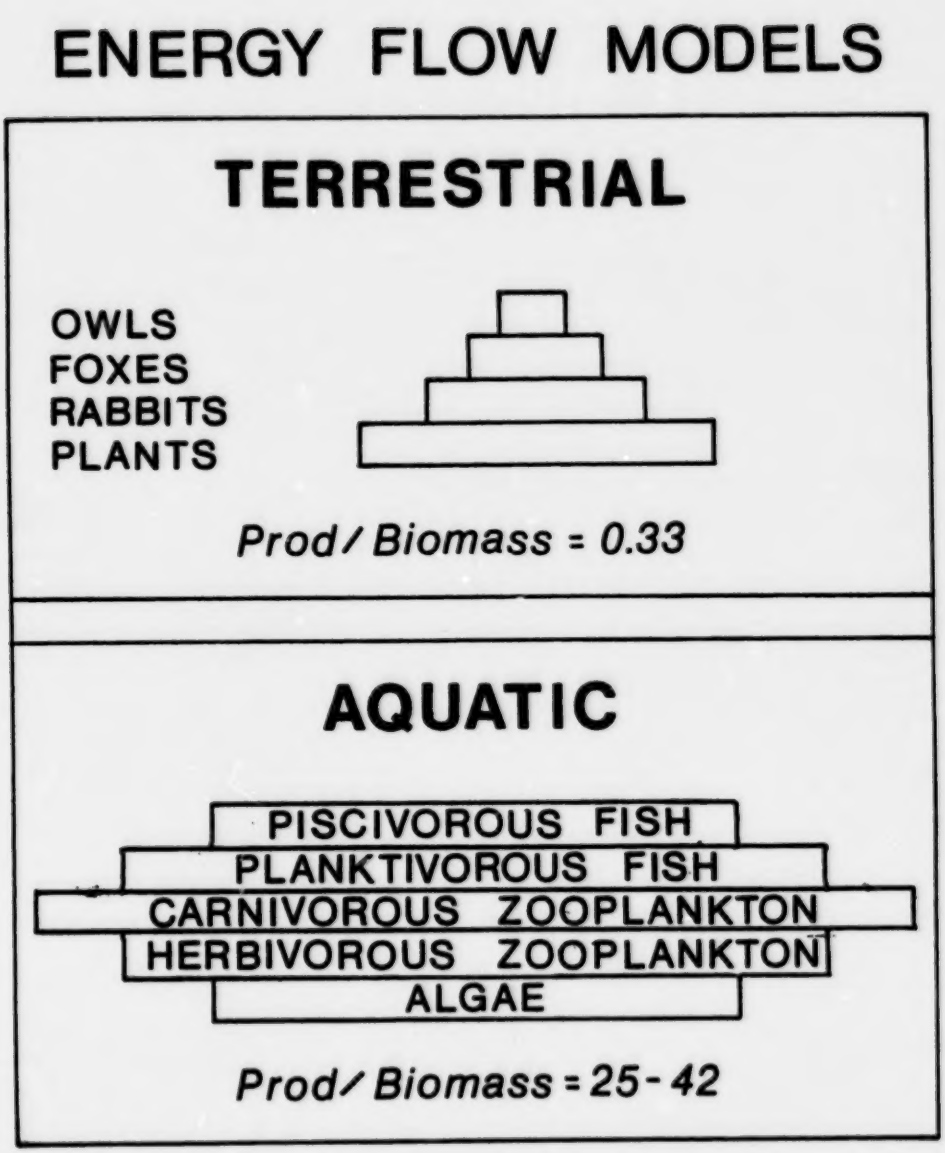

Fig. 6.3. Energy flow models of terrestrial and aquatic ecosystems. Note the different production: biomass ratios as discussed in the text.

CHAPTER 7

FEEDING RELATIONSHIPS PART II:

THE USE OF ECOLOGICAL FOOD WEB MODELS

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INTRODUCTION

Ecologists can make many contributions to the development of contaminant food web models from points of view other than those of mathematical modellers or fisheries biologists. One of those roles is as gadflies, ensuring that components of the ecosystem are all considered in the construction of models, and that the effects of simplifications necessary to construct mathematically tractable models are also considered. The object of model development is to permit predictions of the effects of changes in the ecosystem or the forcing functions on particular components of the system. The objective of food web models in this case, at least in part, is to permit prediction of contaminant burdens in sport fish such as pickerel, pike and bass. There are many models which could be employed to make those predictions, ranging from estimates based only on contaminant levels in sediments and water, through various kinds of simple, linear food chain models, to arbitrarily complex models representing the best available models of interlinked food webs.

Simple models have considerable appeal to those who must construct and test them. More complex models appeal to biologists, who typically believe they better represent interactions in the real world. The usual systems, or box-and-arrow model of a food web represents a compromise between biologically complex reality and computational tractability. To ensure that those who construct box-and-arrow models recognize that these models are usually simplifications of biological reality, a few examples of evidence of the complexity in the biology of one of the target taxa will serve. A survey of the published literature over the 1984 to 1986 period studying the ecology of large and small mouth bass (Micropterus salmoides and dolomieui respectively) indicates a number of ecological and

behavioural complexities difficult to include in a box-and-arrow model of the sort proposed.

SYSTEM COMPLEXITIES

One kind of complexity results from temporal change in the ecology of bass. There is evidence of a consistent pattern of age and/or size dependent shift in the habitat selection of both large and small mouth bass. Each species moves from shallow to deeper water with increasing age (Wanjala et al. 1986, Rankin 1986), and chooses specific bottom types as well. Spatial shifts need not have an impact on the food web model, but in parallel with habitat shifts various diet shifts also occur. Some studies of bass diets include suggestions of a simple correlation between prey size and predator size, indicating shifts in relative abundances of prey species in the diet with predator growth, but continuing use of the same spectrum of prey species. For example, large mouth bass are reported to consume at least some gizzard shad even as young-of-the year, but gizzard shad became the dominant component of the gut contents in later years in Lake Shelbyville, Illinois (Storck 1986). That diet shift could be accommodated in a box-and-arrow model through age-dependent variation in transfer rates. However, in other cases the diet shifts reported are more radical, and represent transfers from completely different boxes at different ages. For example, large mouth bass have been reported to shift from a completely invertebrate diet when young to a completely piscivorous diet as mature adults (Miller and Starck 1984). This complexity could be incorporated by considering different age classes as separate components of the ecosystem, but would require determination of a large number of inter-compartmental transfer rates.

Other complexities are related to spatial variation in the ecosystem

structure and the behavioural responses of bass to those changes. Large mouth bass increase the breadth of their diets in response to increases in the density of aquatic vegetation in a laboratory study (Anderson 1984). This relationship between vegetation and diet was argued to result from the optimization of foraging tactics. Quantitative change in diet breadth is difficult to monitor in the field. Qualitative change, for example, change in preference from one species to another can be apparent in the field. Schramm and Zale (1985) indicate that with a cover of aquatic vegetation large mouth bass prefer bluegills, but in the absence of that cover their preferred food was telapia. Obviously habitat effects will be site specific. However, since adult bass move over a considerable area, and thus a range of habitat conditions, a quantitative estimate of diet could be problematic, and result in errors in the predictions of a contaminant web model.

It seems likely that with sufficient biological data the kinds of temporal and spatial complexity readily evident in the literature relating to the diets of bass will also be found in the relationships among components at all levels of the food web. Further, the details of these complications are likely to show site specific differences. While each of the complexities considered, and this is clearly an incomplete list, make the development of a realistic, quantified box-and-arrow model difficult, they should also make evident the inadequacy of simpler models in their attempts to make accurate predictions.

SYSTEMS MODELS

Have box-and-arrow models been successful? If the answer is limited to attempts to estimate contaminant burdens, I know of no examples. There have, however, been numerous studies developing both mathematical models

and natural evidence for biomagnification. The field data are surprisingly equivocal concerning the widespread occurrence of biomagnification among species and trophic levels. There is general agreement that there is evidence of significant biomagnification of PCB's in higher trophic levels of both terrestrial and aquatic ecosystems. Sparrow hawks had more than 50 times the concentrations of PCB's in tissues of insectivorous birds in England (Presst et al., 1970). Thomann (1981) found contaminant levels of the top predators in aquatic ecosystems were similarly the result of biomagnification. The results of studies of lower trophic levels are much less clear. While biomagnification is tacit evidence of the importance of diet in contaminant uptake, lower trophic levels may accumulate a significant portion of their contaminant burdens through direct exposure, e.g. through uptake from water passing over gill structures in aquatic invertebrates. Many studies do not (and, if direct exposure is the principal route of uptake, should not) show evidence of biomagnification in lower trophic levels (Nisbit and Sarofim 1972, Ellgehausen et al. 1980, Hunter et al. 1980, and Clayton et al. 1977). Taken together these papers have studied a broad range of types of aquatic ecosystems from streams to marine environments.

As a result of the uncertainty concerning the relative importance of dietary and direct environmental exposure to contaminants, mathematical models of the movement of contaminants among components of an ecosystem generally include terms for both sources. Shaw and Connell (1986) review a number of approaches. These approaches, as seems generally the case in contaminant studies, consider food chains, not food webs. They are, therefore, inadequate to model the movement of contaminants through the frequently complex pathways of either terrestrial or aquatic food webs.

This is the point at which ecologists may be able to aid in studies of transfers among compartments in real ecosystems.

In the context of ecological, energetic food webs there are many examples, and many ways in which these can assist in the development of contaminant models. One of the major problems in developing contaminant models is the estimation of transfer rates among compartments. When energetic transfer rates are known, two approaches become possible: 1) Important links in the system can be identified from energetic transfer rates, and the contaminant web model simplified on ecologically justified grounds by excluding unimportant links from the final model. 2) Where contaminant transfer rates may be both difficult and expensive to measure, coarse estimates can be derived from the energetic web. These estimates assume that the lipid content of prey organisms carries an equilibrated concentration of the contaminant under study. If the lipid biomass transferred between boxes (trophic levels, or whatever units are being used in the model) can be estimated, then the contaminant transferred can also be estimated. These estimates are derived from the biomass transfer rates (0_x), the percent lipid content of the prey organism (1_x), and an estimate of the lipofelicity of the contaminant under study, possibly K_{ow}. The transfer rate for the contaminant, estimated from the energetic food web, is then,

$$T = 0_x \times 1_x \times K_{ow} \qquad (1)$$

This approach to estimation is coarse and incomplete. Transfer rates among living components of the ecosystem are, of course, only part of the story. A complete model must include various losses which occur in addition to transfers to higher trophic levels. These include natural death rates, rates of metabolic degradation of contaminants, and excretion

rates. Contaminant movements due to excretion and organism death could be approached by parallel analogies to energetic models. Metabolic degradation has no energetic analogy, and is a complex problem for any method of food web modelling. This method does not necessarily distinguish potentially important species or individual differences in assimilation efficiency. However, it has the advantage of providing estimates necessary to the development of a screening model with relative ease. The necessary parameters have, in many cases, already been measured and published.

Finally, energetic box-and-arrow models have been tested and verified against field measurements. Where simple models have been poor predictors of reality, the complications necessary to improve predictions have been determined and incorporated. Those complications provide useful clues to the difficulties likely to be encountered in developing a useful predictive model for the movement of contaminants through the food web. To see how such models are constructed and corrected, I will review briefly one model of a small lake ecosystem. The basis of this model is Lindeman's studies of Cedar Bog Lake (Linkeman 1941, 1942), in which much of the basic approach and terminology of trophic energy was developed. This trophic structure was quantified in a form useful to the development of contaminant web models by Williams (1971).

Williams developed the final model in three stages. The first stage reiterated the three-level trophic structure consisting of compartments for plants including all photosynthetic organisms, herbivores and carnivores. For each compartment 1) input, 2) transfer to the level above, 3) respiratory loss, and 4) unspecified other losses (including

principally death) are balanced to bring the system to equilibrium. Each rate of transfer out from a box is linearly related to the standing crop of that compartment. The simple linear model which resulted did not accurately reflect the dynamics of measured standing crops. Therefore, Williams constructed a more detailed, 10-compartment model of the trophic structure of Cedar Bog Lake.

To quantify the standing crops and transfer rates for the 10 compartment model of Cedar Bog Lake, Williams had to make many assumptions, particularly about benthic components and the active layer of the sediment. The compartment sizes and flow rates when the differential equations describing the system had been solved for equilibrium conditions, could be used to assess the relative importance of different pathways (see Fig. 7.1). The largest compartment by a factor of approximately 50 is benthic plants. By virtue of that size, benthic plants are the chief contributors to the organic fraction of the ooze. Through indirect links the benthic plants are, therefore, important contributors to higher trophic levels. Major pathways from the ooze lead to upper trophic levels, e.g. piscivorous fish, by way of zooplankton and browsing herbivores. Both of these compartments received their largest inputs from the ooze. Other features evident in this web include differences in the major predators of nannoplankton (zooplankton predominate) and net plankton (plankton predators predominate). This additional complexity still did not accurately predict the dynamics of standing crops in the compartments.

To accurately portray those dynamics a third model, much like the second, but incorporating non-linearities in the responses of some compartments (e.g. self-inhibition or competition in the dynamics of plant

and swimming predator compartments), differences in the temperature dependence (Q_{10}) of responses of some compartments and the incorporation of seasonal cycles in the solar energy input and in the responses of some compartments produced a model which fit observed dynamics reasonably well.

CONCLUDING COMMENT

What have these complications demonstrated? A predictive model of the trophic web for Cedar Bog Lake had to incorporate a variety of realistic biological corrections, both in terms of the number and relationship of compartments, and in the internal dynamics of those compoartments, i.e. self-inhibition, to accurately model the dynamics of the ecosystem as a whole. The assumption that simple serial models can adequately predict the dynamics of contaminants in aquatic ecosystems is fraught with danger. Realistic models are usually, though unfortunately, realistically complex.

REFERENCES

Anderson, O., (1984). Ecology, 65:851.

Clayton, J.R., Pavlou, S.P., and Brietner, N.F., (1977). Environ. Sci. Technol., 11:676.

Ellgehausen, G., Guth, G.A., and Esser, H.O., (1980). Ecotoxicol. Environ. Safety, 4:134.

Hunter, R.G., Randolph, J.C., Carroll, J.H., (1980). Environ. Pollut. B, 1:233.

Lindeman, R.L., (1941). Amer. Midl. Natur., 26:636.

Lindeman, R.L., (1942). Ecology, 23:399–418.

Miller, S.J., and Strock, T.W., (1984). Trans. Am. Fish. Soc., 113:571.

Nisbit, I.C.T., and Sarofim, A.F., (1972). Environ. Health Perspect., 1:21.

Presst, I., Jeffries, D.J., and Moore, N.W., (1970). Environ. Pollut., 1:3.

Rankin, E.T., (1986). Trans. Am. Fish. Soc., 115:322–334.

Schramm, H.L., and Zale, A.V., (1985). Trans. Am. Fish. Soc., 114:725–731.

Shaw, G.R., Connell. D.W., (1986). PCBs and the Environment, Vol. 1, J.S. Waid (ed.), CRC Press, Boca Raton, Fl., 135–142.

Storck, T.W., (1986). Trans. Am. Fish. Soc., 115:21–27.

Thomann, R.V., (1981). Can. J. Fish. Aquat. Sci., 38:280.

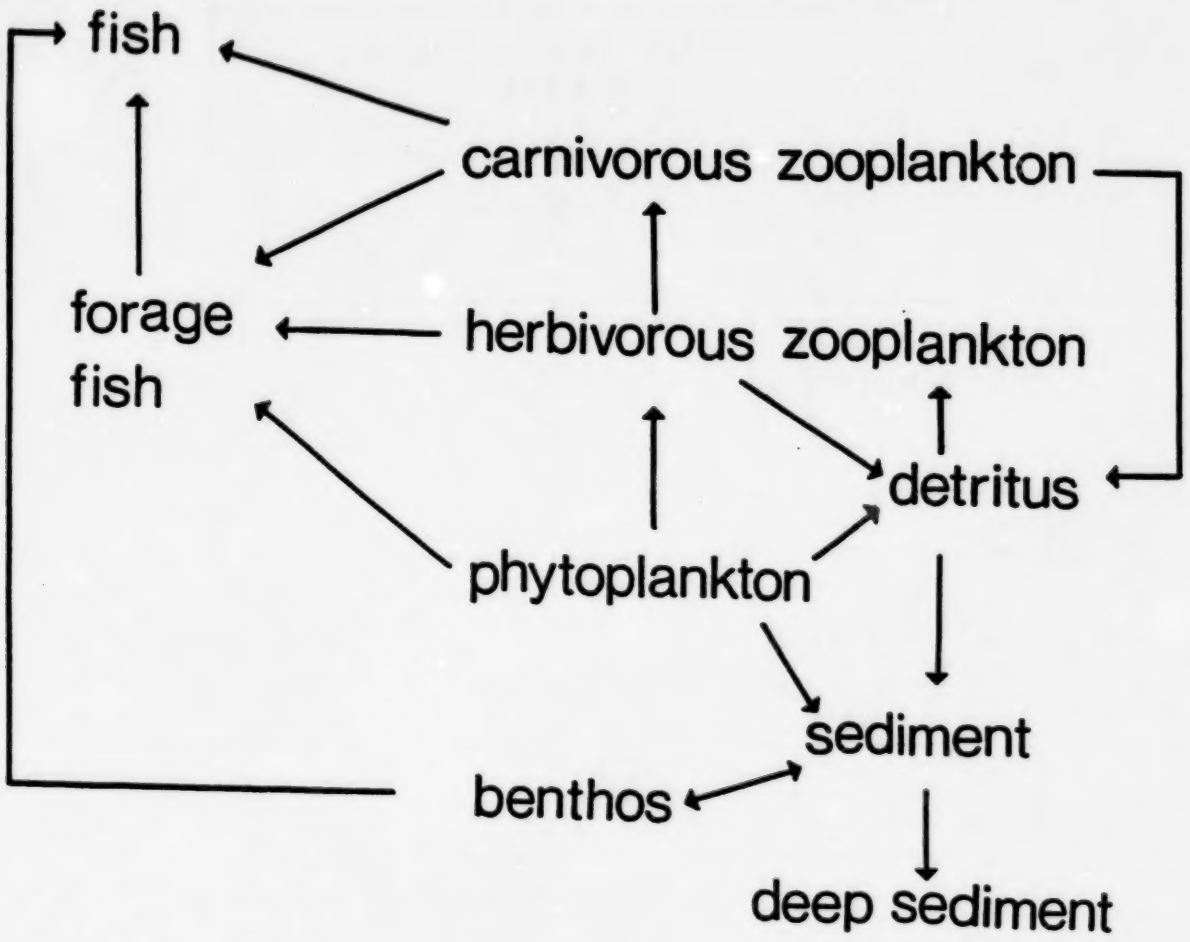
FIGURE CAPTIONS

Fig. 7.1. Food web energy flows.

Fig. 7.2. Major compartments and pathways in the Cedar Bog Lake ecosystem. For compartment sizes and non-linear equilibrium flow rates see Williams (1971).

FIG. 7.1

FOOD WEB ENERGY FLOWS



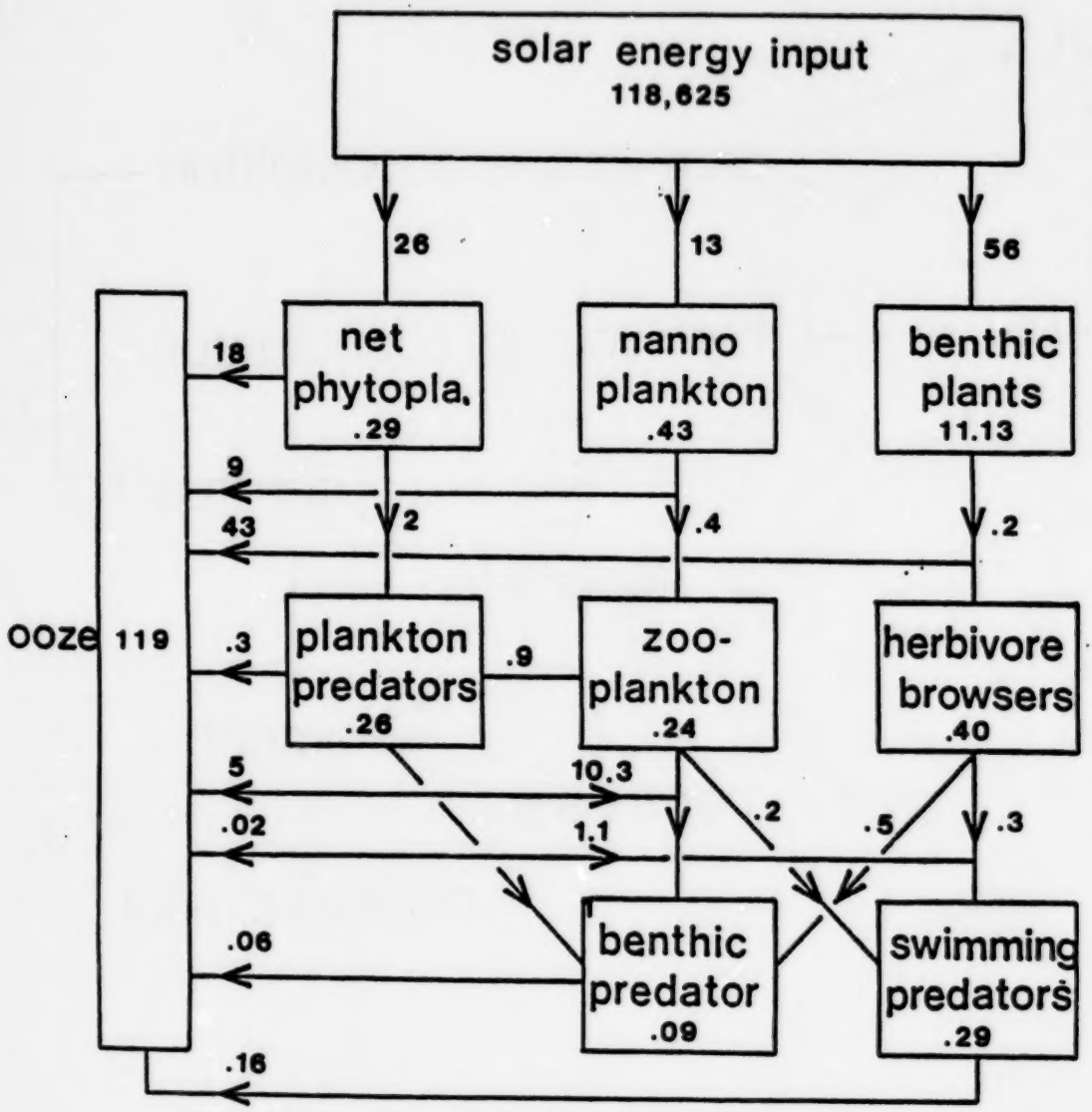


FIG. 7.2 Major compartments and pathways in the Cedar Bog Lake ecosystem. For compartment sizes and non-linear equilibrium flow rates see Williams (1971).

CHAPTER 8

SUMMARY OF FINDINGS AND RESEARCH NEEDS

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SUMMARY OF FINDINGS

The synopsis of the deliberation of the work groups as reported by the respective coordinators is attached in Appendix B. The major findings are:

- The chemical classification based on K_{ow} (the octanol water partition coefficient) can be used to assist in the selection of the appropriate model for estimating contaminant levels in biota.

FOOD CHAIN/CHEMICAL CLASSIFICATION

Log K_{ow}	Suggested Model	Reference
< 5	Only phase partitioning required. Lipid normalization useful. Suggested screening model $\nu = (K_{ow})$(lipid fraction) c.	R. Thomann (Chap. 3) D. Mackay (Chap. 4)
5 - 7	Food chain model needed. Generic models are useful for screening. Site- and species-specific models are very data-intensive and are in the initial stages of development.	
> 7	Knowledge base is too uncertain for reliable modelling.	

- A simple four box generic food chain model as shown in Fig. 8.1 is a useful screening tool that accounts for uptake from the water column and the lower trophic levels. This model is an improvement over a single BCF computation without the vast data requirement for a site specific food chain model. This model, however, can be used as a screening tool to provide a relatively rapid assessment for problem identification, setting priorities and planning further studies. A site- and species-specific model is needed in the event that models are to be used as regulatory tools.

- A pathway model as shown in Fig. 8.2 which includes a pelagic food web (phytoplankton, zooplankton, larval fish, forage fish and piscivorous) and a benthic food web (benthic invertebrates and benthic fish) may be used as part of an advanced approach to estimate contaminant levels in the ecosystem.

- The tentative diet for the generic groups shown in Table 8.1 and Fig. 8.2 provides insight into the type of data needed to ensure a proper computer model that includes the general pathways and coupling as illustrated in Fig. 8.2. When site- and species-specific data become available, this generic model can be upgraded and calibrated for the site under consideration.

RESEARCH NEEDS

During the work group seminars and the formal presentations, several information gaps were identified as being important to the development of a biologically reliable model for estimating the contaminant body burdens in aquatic biota.

In order to represent the impact of a proposed contaminant load on the biota at a particular site, it is essential that a dynamic site and species model be developed. At present this type of model is at the research stage. As a research tool the generic pathways can serve as a useful initial framework for the development of a calibrated and verified species-specific model. In order to achieve this goal there are information gaps that need to be filled.

Bioavailability has been shown to be important in the uptake of metals. Dr. Thomann indicated that bioavailability may also be important in membrane transfer. Normally, dissolved contaminants are available for transfer across a biological membrane; however, if the contaminant is associated with another dissolved chemical, especially a dissolved organic carbon (DOC), it may not move through the membrane of the organism as readily. Dr. Bierman discussed the importance of bioavailability in the interstitial water of sediments. More research is required to determine the site-specific factors that influence the bioavailability of various pollutants. Predictive equations are required for modelling purposes.

The workshop identified gut content data as one of the major information gaps for the Great Lakes System. This information is required for all potential impact areas within the Great Lakes System. From this information, both diet and contaminant pathways can be established. One of the outstanding modelling concerns that this information would help to answer is the relationship between the pelagic and benthic food chains. A considerable amount of attention in the work groups was focused on the applicability of size classification. More research is required to determine the usefulness of this concept in pelagic and/or benthic food chain models. Another information gap is the lack of a complete body burden data set for a few sites covering spatial, temporal and age variations of important species. This information is required for model calibration.

The role of biota in the mass balance of contaminants in aquatic systems is not well understood. Special attention needs to be directed to defining the roles of macrophytes in the uptake, storage, transfer and release of contaminants. In addition, the importance of export due to emergence and harvesting on the mass balance needs to be quantified.

Our knowledge base for the fate and uptake of contaminants with high K_{ow}'s ($\log K_{ow} > 7$) is very limited. Dr. Mackay and his group have determined that these contaminants behave in a distinctive way and cannot be modelled adequately by the existing food chain models. This is an important area needing fundamental research.

The total impact of a given discharge depends on the combined effects of all the contaminants in the effluent. Research into whole effluent modelling should be pursued. A starting point in this effort is the work of DiToro (1984) in which he considered modelling LC50 as a load.

The processes involved in the contaminant transfer from the effluent to the various trophic levels of the food chain are stochastic. There is a need to consider this stochastic nature in the modelling process.

The accumulation of contaminants in fish depends on factors which are at present inadequately quantified. More research is required to determine the functional relationships for: growth rates of both benthic and piscivorous fish; respiration rates for fish; assimilation efficiency for food and contaminants; excretion and depuration rates for aquatic biota.

REFERENCES

DiToro, D., (1985). "New Approaches to Contaminant Modelling", UGLCCS Modelling Workshop, GLERL, Ann Arbor, December 3.

Table 8.1 FOODCHAIN DIET DISTRIBUTION IN PERCENT

					CONSUMERS				
	ORG.	MACRO-	PLANKTON		BENTHIC	FISH			
FOOD	DET.	PYTES	PHYTO	ZOO	INV.	LARVAL	FORAGE	PISC	BOTTOM
ORGANIC DETRITUS					40				40
MACRO-PHYTES					15			5	10
PHYTI-PLANKTON			100		15	5	10		
ZOOPLANK-TON					20	85	65	5	
BENTHIC INV.									50
LARVAL FISH						10	25	20	
FORAGE FISH								60	
PISC. FISH								10	
BOTTOM FISH									

FIGURE CAPTIONS

Fig. 8.1. Simplified generic food chain.

Fig. 8.2. Suggested aquatic food chain.

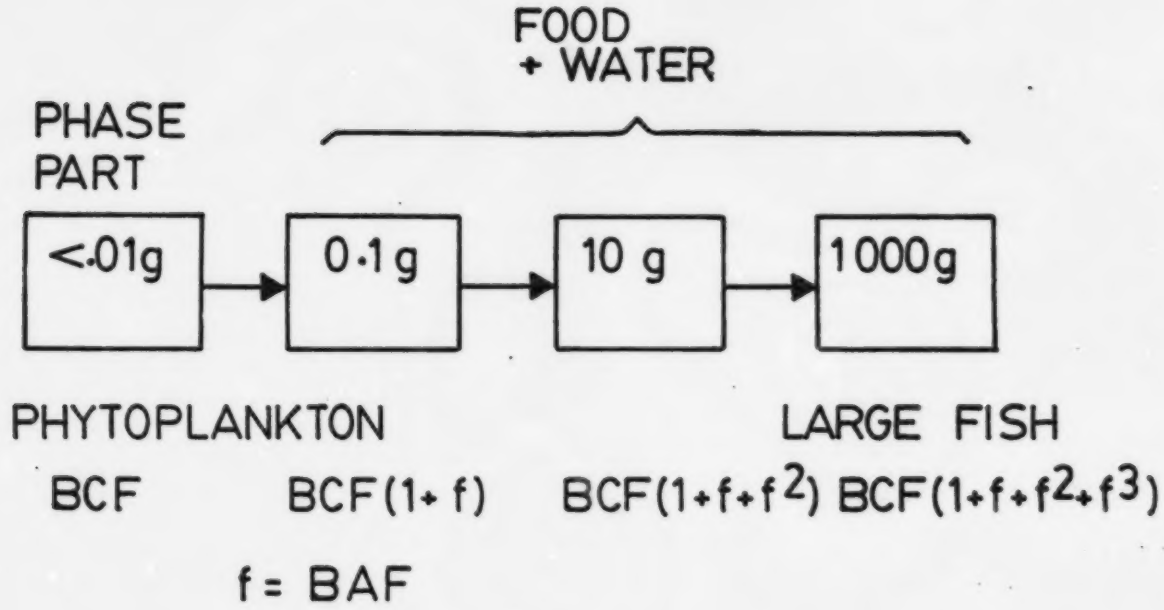

FIG. 8.1 Simplified Generic Food Chain

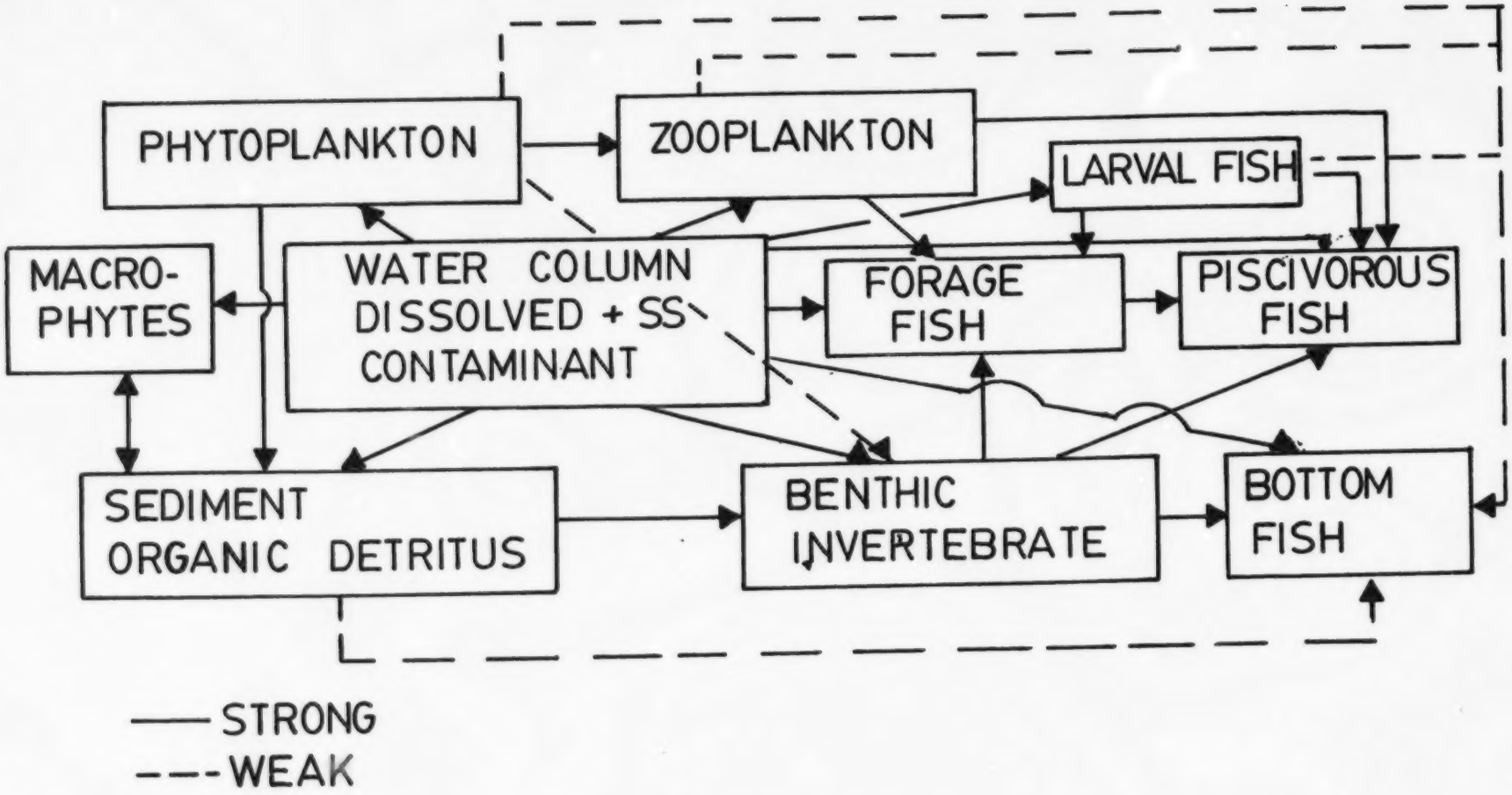

FIG. 8.2 Suggested Aquatic Food Chain

APPENDIX A

1. WORKSHOP AGENDA
2. LIST OF PARTICIPANTS
3. GENERAL AND SPECIFIC QUESTIONS

AGENDA

AQUATIC FOOD CHAIN MODELLING WORKSHOP

THURSDAY, JULY 9

10:00 AM	Welcome, and opening remarks (Y. Hamdy - Ontario MOE)
10:15 AM	MISA Water Quality Track (C.F. Schenk - Ontario MOE)
10:30 AM	Food Chain Modelling Framework - Purposes and Applications (J.A. McCorquodale - U. of Windsor)
11:00 AM	Food Chain Modelling Concepts and Requirements (R.V. Thomann - Manhattan College)
12:00 NOON	Lunch Break
1:00 PM	Sediment Interactions with the Biotic and Abiotic Solids in the Water Column (V. Bierman - Notre Dame University)
1:30 PM	Feeding Relationships (D. Haffner/M. Weiss - U of Windsor)
2:00 PM	Uptake Kinetics (D. Mackay - Univeristy of Toronto)
2:30 PM	Coffee Break
2:45 PM	Work Group Orientation
3:00 PM	Work Group Sessions: i) Fisheries ii) Plankton iii) Benthos/Sediment iv) Macrophytes
5:00 PM	Dinner
7:00 PM	Work Group Session (cont'd)
9:00 PM	Adjourn for the day

FRIDAY, JULY 10

8:00 AM	Meeting of Work Group Coordinators
9:00 AM	Summary and Discussion of Work Group Sessions: i) Fisheries ii) Plankton
10:00 AM	Coffee Break
10:30 AM	Summary and Discussion of Work Group Sessions (cont'd): iii) Benthos/Sediment iv) Macrophytes/Cladophora
11:30 AM	Overall Summary and Conclusions of Work Shop (J.A. McCorquodale - U. of Windsor)
12:00 NOON	Lunch (optional)

WORK GROUP SESSIONS

July 9-10, 1987

Benthos/Sediment (Room 111)

Coordinators: V. Bierman
W. Scheider

Participants: D. Andrews, D. Boyd, M. Diamond, G. Johnson, D. Mackay, D. Persaud, D. Poulton, W. Wager, L. Wong, M. Jackson, B. Parker, A. Rodrigues, M. Weiss, S. Thornley, M. Kirby

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Fisheries (Room 302)

Coordinators: J. Leach
R. Thomann

Participants: F. Gobas, S. Klose, J. MacLean, D. Rokosh, A. Roy, B. Keller, B. Shuter, G. Westlake, K. Clarke

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Plankton (Room 314)

Coordinators: D. Haffner
P. Nettleton

Participants: S. Abernathy, M. Griffiths, P. Kauss, A. McLarty, N. Yan, E. M. Yuen, Z. Novak

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Note:

Macrophytes will be discussed as part of the benthos/sediment work group session.

Y. Hamdy and J.A. McCorquodale will participate in each session to ensure continuity.

LIST OF MODELS USED FOR SCREENING

A. HYDRODYNAMIC MODELS (WATER-COLUMN SCREENING ONLY)

1. VARIOUS DILUTION/PLUME MODELS
2. KE MODEL - STEADY, 2-D DEPTH-AVERAGED FOR LARGE RIVERS
3. FE MODEL - STEADY, 3-D FOR EMBAYMENTS/LAKES
4. RAND MODEL - UNSTEADY, 2-D FOR LAKES
5. SPILL MODEL - LAGRANGIAN, 2-D.

B. FATE & TRANSPORT (WATER-COLUMN, SEDIMENT, AND TARGET BIOTA SCREENING)

1. TOXIWASP - PRIMARILY ORGANICS
2. WASTOX - PRIMARILY ORGANICS, WITH FOOD-CHAIN
3. MEXAMS/MINTEQ - METALS

INPUT DATA NECESSARY FOR SCREENING A CONTAMINANT SOURCE

(FOR WATER COLUMN/SEDIMENT/TARGET BIOTA CRITERIA)

1. HYDRODYNAMIC

   - STOCHASTIC SUMMARY FOR THE DISCHARGE/STAGE OF THE RECEIVER.
   - CURRENT VELOCITY MEASUREMENTS FOR CALIBRATION OF HYDRODYNAMIC MODEL.

2. EFFLUENT LOADING

   - BAT (EA) CRITERIA INCLUDING BOTH CONCENTRATIONS AND FLOW RATE.

3. PARTITIONING RELATED COEFFICIENTS

   - KOW/KOC
   - ORGANIC CARBON CONTENTS OF SEDIMENT AND TARGET BIOTA.

4. APPROXIMATE SEDIMENT DYNAMICS

   - SEDIMENT CONCENTRATIONS IN WATER COLUMN AND BED
   - SEDIMENT LOADS FROM OUTFALLS/OTHER

5. MEASURED AMBIENT CONCENTRATIONS

   - IN WATER COLUMN/BED/TARGET BIOTA, ALONG WITH LOADING HISTORY, FOR MODEL CALIBRATION.

FATE AND TRANSPORT MODEL: TOXIWASP

Field-acquired input data for modelling are:

1. Particle-size distribution of suspended solids, bed sediment, and bed load.
2. In-place density of bed sediment.
3. Turbidity
4. Bed load transport rate.
5. Pore water percolation rate.
6. Concentrations of total contaminant and suspended solids throughout system (as initial conditions).
7. Concentrations of total contaminant and suspended solids entering river via upstream boundary.
8. All point-source and non-point source loading rates of total contaminant and suspended solids, of signficance.
9. Hydrogen ion-hydroxide in activities (pH-pOH).
10. Concentrations of environmental oxidants (e.g.peroxy radicals) in water and sediment.
11. Organic carbon content of sediments as fraction of dry weight.
12. Organic carbon content of the compartment biomass as a fraction of dry weight.
13. Free electron activity (Eh).
14. Concentration of major anions in water, (CO_3^{2-}, SO_4^{2-}, etc.
15. Concentration of major cations in water, (Ca^{2+}, Mg^{2+}, etc.).
16. Alkalinity.
17. Mineralogical composition of sediments, ($Si\ O_2$, $A/_2O_2$, Fe_2, O_3, MgO, CaO, NaO_2, K_2O, TiO_2, MnO, P_2O_5, etc.)
18. Concentration of Trace Constitutents, (H^2 S, Iron, Manganese, PO_4^-, F^-, Al^{3+}, Ba^{2+}, Sr^{2+}, Cs^+, Li^+, Br^-, NH_4^+, B, Rb^+, I^-, NO_3^-, etc.).
19. Concentration of Inorganic Carbon.
20. Specific Conductivity.
21. Bacterial population density, (both, water and sediment).
22. Total, actively sorbing biomass.
23. Total contaminant concentrations in specific water column and benthic biota, (phytoplankton, zooplankton, young-of-the-year fish, sport fish).
24. Temperature (water).
25. Wind velocity, 10 cm above water surface.
26. Average Cloudiness, (in tenths of full sky cover).
27. Hydrodynamic characteristics.

FOOD \ CONSUMERS	ORG. DET.	MACRO-PHYTES	PLANKTON		BENTHIC INV.	SMALL FISH (P)	LARGE FISH (P)	BOTTOM FISH
			PHYTO-	ZOO-				
ORGANIC DETRITUS								
MACRO-PHYTES								
PHYTO-								
ZOO-								
BENTHIC								
SMALL FISH								
LARGE FISH								
BOTTOM FISH								

1 EXPOSURE CONCENTRATIONS
-DISSOLVED
-SORBED
2 FOOD WEB
PREDATOR - PREY
(BY AGE & SEASON)
3 CONSUMPTION,
4 ASSIMILATION
-FOOD
-TOXICS
5 GROWTH RATE
6 WET/DRY WEIGHT & LIPID CONTENT
7 EXCRETION
8 RESPIRATION
9 BCF
10 BAF
11 MOBILITY/MIGRATION/SPAWNING
12 HARVESTING/REMOVAL
13 DEATH & RECYCLING
14 BIOTURBATION
15 FEEDBACK TO EXPOSURE MODEL
16 METABOLISM

BENTHOS

1. EFFECT OF BENTHOS ON PHYSICAL - CHEMICAL PROPERTIES ?

2. EFFECT OF SEDIMENT EXPOSURES ON BENTHOS ?

3. COUPLING OF BENTHIC AND PELAGIC FOOD CHAINS ?

4. KEY SPECIES IN RELATIONS TO FISH - GUT CONTENTS ?

5. ROLE OF MACROPHYTES IN FOOD CHAIN ?

FISH

1. BIOLOGY :

e.g. - FISH PRED-PREY
- GROWTH
- RESPIRATION
- ASSIMULATION
- HABITATION
- SPAWNING
.
.
.

2. CHEMICAL FACTORS

e.g. BCF
.
.
.

PLANKTON

1. EFFECT OF PLANKTON ON PHASE PARTITIONING ?

   - SEASONALITY ?

   - BIOMASS ?

2. ASSUMPTIONS OF LUMPING/SPLITTING ?

   (NANO vs NET PHYTO)

   (ZOO HERB vs CARN)

3. IMPORTANCE OF PHYTO BCF ON FOOD CHAIN ?

4. IMPORTANCE OF ZOO BCF/BAF ON FOOD CHAIN ?

WORK GROUP

GENERAL :

1. EXAMINE PATHWAY SYSTEM DIAGRAM AS A GENERIC MODEL IN CONTEXT OF GREAT LAKES AND RIVERS.

   - COMMENT ON ITS SUITABILITY.

2. SUGGEST AGE/SIZE CLASSIFICATION AND ASSOCIATED PATHWAYS.

3. IDENTIFY IMPORTANT PATHWAYS AND SPECIES IN PATHWAY - WHAT ASSUMPTIONS ARE IMPLIED IN THESE SIMPLIFICATIONS ?

4. COMPLETE CONSUMER FOOD MATRIX - INCLUDING REPRESENTATIVE DISTRIBUTION OF DIET.

5. CHANGES NECESSARY TO UPGRADE GENERIC MODEL TO DERIVE A SPECIES SPECIFIC MODEL.

6. MAJOR GAPS IN INFORMATION HINDERING FOOD CHAIN IMPLEMENTATION.

APPENDIX B

WORK GROUP REPORTS

AQUATIC FOOD CHAIN MODELLING WORKSHOP

SUMMARY OF DISCUSSIONS OF FISHERIES WORK GROUP

COORDINATORS: J. Leach
R.V. Thomann

PARTICIPANTS:

F. Gobas	S Klose
J. MacLean	D. Rokosh
A. Roy	B. Shuter
G. Westlake	K. Clarke

OPENING DISCUSSION

The initial discussion of this workgroup centered around the issue of global versus specific type models of the aquatic ecosystem and the transfer of chemicals within that ecosystem. The participants reviewed the advantages and disadvantages of each direction. For global models, the degree of simplification is appealing since global models are therefore useful for screening type of activities where specific chemicals are to be evaluated on a broad non-site specific basis. On the other hand, global models do not provide specific details on individual sites and therefore are not useful for individual waste load allocation purposes.

The present structure of the MISA program was reviewed and the issue of having guidelines for chemical concentrations in top predators was discussed. It was pointed out that some of the most significant impacts of toxic chemical discharges has been the closing of fisheries because of elevated concentrations in the top predator fish and subsequent presumed public health impacts if such fish are consumed.

APPROACH FROM TYPE OF CHEMICAL

Following these opening discussions, the work group addressed the question of whether food chain modelling was required at all. As a result of this basic question, the group looked at dividing the chemicals under consideration using the octanol water partition coefficient (K_{ow}) as an ordering parameter. Thus the chemical population was divided into three broad groups:

$\log K_{ow} < 5$

$\log K_{ow} = 5$ to 7

$\log K_{ow} > 7$

This division of chemicals (where the bounds of such divisions are somewhat approximate) reflect recent work on the significance of food chain transfer of chemicals and subsequent accumulation up to the top predators. At $\log K_{ow} < 5$, food chaim accumulation is generally small. At $\log K_{ow} = 5$ to 7, food chain effects begin to become important and for $\log K_{ow} > 7$, there is uncertainty as to the actual significance of food chain transfers. (Summary papers presented at the workshop explored these concepts in greater detail.)

Chemicals with $\log K_{ow} < 5$

For this group of chemicals, the discussion reviewed the possibility of dealing with such chemicals using a simple lipid partitioning concept. Thus, the concentration of the chemical in a fish or any other organism on a lipid basis would be given by:

$$\nu = K_{ow}\, pc \qquad (1)$$

where

ν = chemical concentration in the organism ($\mu g/kg$ (ℓp))

p = the fraction lipid weight, and

c = the water concentration ($\mu g/L$)

In this equation, it is assumed that K_{ow} is an accurate measure of the partitioning of the chemical into the lipids of the organism.

The procedure then for these chemicals is therefore quite simple. An estimate must be made of the K_{ow} and the fraction lipid of the organism. (It was suggested after some discussion that for screening purposes, a conservative value of perhaps 0.20 should be used. For site specific situations, the lipid fraction for individual species should be used.)

If a guideline for the chemical concentration is available then the above equation is solved for the allowable water concentration, i.e.

$$c = \frac{\mu_\epsilon}{K_{ow}} p \qquad (2)$$

where

μ_ϵ = the guideline chemical concentration in the organism

If this concentration is greater than any other concentration determined from, for example, acute and chronic effects considerations on the ecosystem, then the guideline for the chemical concentration in the organisms is not controlling. If however, the water concentration calculated from the latter equation is less than any other water concentration obtained from other considerations, then the organism is controlling.

Chemicals with log K_{ow} > 7

This group of chemicals was dealt with rapidly. It was concluded that not enough information was available to fully assess the potential for chemicals in this range to bioaccumulate. There is some evidence and theoretical justification for believing that chemicals with high K_{ow} (> 7) would not continue to bioaccumulate.

However, the general consensus was that this area is a major information gap and needs to be evaluated with field and laboratory research and applications efforts. If a specific request is received to discharge such chemicals, it was felt that the burden should be placed on the discharger to develop the data base necessary to justify the discharge.

Chemicals with log K_{ow} 5 to 7

Since this group of chemicals has the most potential for some bioaccumulation, discussions centered about the appropriate model structures that could be used. Attempts at expanding the food chain structure provided to the group were not successful. It was felt that increasing the complexity of a generic model did serve any particular value although there was some disagreement in the group over this point. Eventually, the group concluded that it could not assign generic values to the various elements of a food chain model and opted in the direction of more site specific models.

The basic hesitation in further expanding generic models was the concern that such analyses would drive the permitting process. It was pointed out that all of the modelling frameworks, whatever their level of detail were intended mainly as analyses that would provide information to the decision making process, but not dictate that process.

A general consensus emerged supporting the application of existing food chain modelling structures to specific case studies in order to gain expertise in the use of such models.

The suggestion was made also that perhaps the easiest approach was to calculate the chemical concentration in the top predator by simply applying a multiplier of 10–1000 times the concentration that would occur

from exposure to the water only. Discussion indicated that there would be some significant difficulty in picking the multiplier. It was also indicated in subsequent discussion that such a multiplier is in fact capable of being computed from a relatively simple generic four-level food chain model.

In conclusion, the group:

1. was split on the utility of generic models;
2. developed a consensus on applying food chain models to site specific case studies;
3. suggested several approaches for calculating chemical concentration in the log K_{ow} range of 5-7 including simple multiplier, or a simple four level generic model;
4. expressed through several individuals, reservations about the utility of such modelling efforts in the decision making process and proposed instead a more specific, case by case qualitative and semi-quantitative determination of the importance of chemical transfers in the food chain.

AQUATIC FOOD CHAIN MODELLING WORKSHOP BENTHOS/SEDIMENT SUBGROUP

COORDINATORS:	V. Bierman	University of Notre Dame
	W. Scheider	Ministry of the Environment
PARTICIPANTS:	D. Andrews	Ministry of the Environment
	M. Diamond	University of Toronto
	D. Mackay	University of Toronto
	D. Poulton	Ministry of the Environment
	L. Wong	University of Windsor
	B. Parker	Ontario Hydro
	M. Weiss	University of Windsor
	D. Boyd	Ministry of the Environment
	G. Johnson	Ministry of the Environment
	D. Persaud	Ministry of the Environment
	W. Wager	Ministry of the Environment
	A. Rodrigues	Ministry of the Environment
	S. Thornley	Ministry of the Environment
	M. Kirby	Ministry of the Environment

The Benthic/Sediment subgroup met the afternoon and evening of July 9, 1987, charged with addressing the six general questions posed to each group as well as five questions specific to the subgroup. After initial discussions which focused on the uncertainty surrounding the use of food chain models, (how will they be used, under what conditions are they to be used) the group split into two subgroups, along the lines of expertise in sediment chemistry vs biology. The "sediment chemistry" subgroup was chaired by V. Bierman and the "biology" subgroup by W. Scheider. The two subgroups rejoined in the evening and the following is a summary of the points discussed. Most of the questions the group was charged with addressing were touched on.

(i) The group consensus was that there is a coupling between benthic and pelagic food chains. The manner of coupling is shown in a generic way in Fig. B-1. Figure B-1 was suggested as the basis for developing a generic food chain model in the Great Lakes and

interconnecting channels. To develop a site specific model, much more information would be necessary.

(ii) The group proposed a consumer food matrix as shown in Table B-1. The matrix was a generic one and more information would be needed to apply the matrix to a specific site. The matrix will vary with the age of organisms (especially fish), species of organism and season as well as by site.

(iii) Major gaps in formation hindering the development of a model to address contaminant transfer in the food chain were identified as:

- lack of information on the role of macrophytes - to what extent do they take up contaminants from the sediment?
- lack of information on food sources of biota (more gut content data needed)
- lack of information on rate constants pertaining to transfer rates between components of food chain
- lack of information (or perhaps a synthesis of information) on contaminant burdens in components of the food chain
- lack of information on the importance of microbially mediated transfer processes
- validation of any site specific model is needed before confidence can be placed in it.

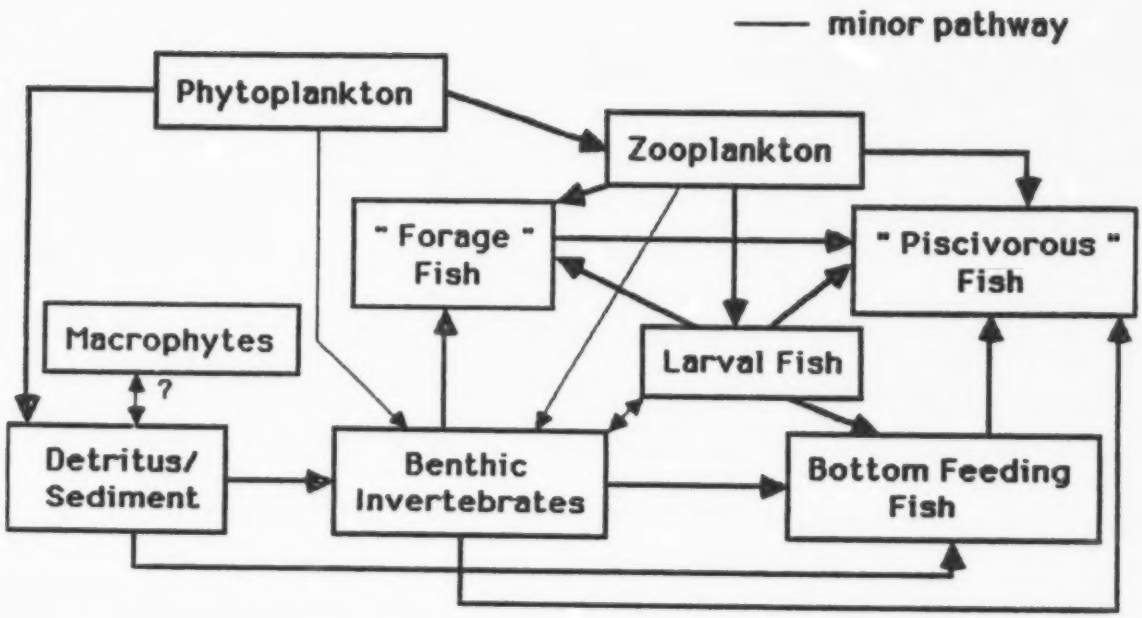
Table B.1

Generic Consumer Food Matrix

	Consumer (figures are % diet)								
	Det.	Macro.	Phyto.	Zoopl.	Benthos.	Larval F.	Forage F.	Bottom F.	Pisc. F.
Detritus	-	-	-	-	40	-	-	40	-
Macrophytes	-	-	-	-	15	-	-	10	-
Phytoplankton	-	-	-	100	15	5	10	-	-
Zooplankton	-	-	-	-	25	85	65	-	5
Benthos	-	-	-	-	-	10	25	50	20
Larval Fish	-	-	-	-	5	-	-	-	-
Forage Fish	-	-	-	-	-	-	-	-	65
Bottom feeders	-	-	-	-	-	-	-	-	10
Piscivorous fish	-	-	-	-	-	-	-	-	-

Figure B.1

Contaminant Movement in a Foodchain



Note: Contaminants dissolved in water move to all "boxes".

Contaminants in the particulate form in water move to the sediment.

Macrophytes are submergent communities (emergents can get contaminants from the atmosphere).

This generic model is more applicable to organics than metals.

AQUATIC FOOD CHAIN MODELLING WORKSHOP

COORDINATORS: D. Haffner
P. Nettleton

PARTICIPANTS: S. Abernathy
P. Kauss
E.M. Yuen
Z. Novak
M. Griffiths
A. McLarty
N. Yan

GENERAL

Plankton

1. Effect of plankton on phase partitioning was considered to be very important and very dependent on the composition of the flora and fauna. Many plankton forms have mucilage and oil storage products, and considering the rapid turnover time (days) would possibly represent a key component in the phase partitioning of contaminants in the aquatic environment.

2. Questions of lumping and splitting species, size groups, functions, habitats would be reduced if a size classification model were accepted by the MOE.

3 & 4. As noted in 1 above, one cannot overemphasize the importance of phytoplankton and zooplankton on bioconcentration factors and bioaccumulation factors. As noted in the Lake Michigan model, this can be the controlling step.

The following are the reponses for this group to the general questions posed in Appendix A:

Question 1. The work group preferred to avoid using food web or food chain models, but recommended size class as developed by Kerr and Sheldon.

Question 2. Size classification models as recommended above avoid porblems with age (e.g. species moving from one compartment to another)

and simplify the relationship between size class intervals. Food web approaches were thought to be much too complicated for any real solution.

Question 3. Pathway and species problems are minimized using the approach recommended. In food webs, how do you know important pathways with respect to both the constancy and persistence of populations. They are probably quite different or at least operate on different scales.

Question 4. Group declined to provide estimates.

Question 5. After much discussion the group recommended research be oriented towards developing a hybrid of a size classification model (to the level of zooplankton) and food web model (forage fish to predator fish). This should provide managers with information on the response of contaminants in fish to a given control program.

Question 6. Major gaps in information hindering food chain implements were:

(a) lack of knowledge at level of species

(b) seasonality

(c) gut content

(d) surface films

(e) sediment-water flux

(f) water-atom flux

(g) migration

(h) feeding habits